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LIGHT DISTRIBUTION IN OPTICAL SYSTEMS

By P. G. Nutting

A comprehensive review of the fundamental principles of photometry, illustrated by numerous practical applications to the simpler photometric surfaces was published by the late Dr. Rosa in 1910.[1] Since that period our knowledge of photometric units and nomenclature has been further crystallized and extended as outlined in the 1919 report of the Standards Committee on Photometry and Illumination of this Society. The International Commission on Illumination, meeting in Paris in July, 1921, has adopted[2] definitions of three fundamental photometric quantities, which are as clear and explicit as could be desired. It therefore appears to be a fit time to extend the earlier treatment of photometric principles to cover optical systems in general, special attention being given to those systems in which the ultimate photometric surface forms part of either a visual or a photographic system. A treatment that is at once simple, exact, and comprehensive is much needed for reference.

Fundamental Definitions, Units, and Nomenclature

Four photometric quantities are commonly accepted as fundamental: (1) luminous flux, (2) flux per unit area, (3) flux per unit solid angle, and (4) flux per unit solid angle per unit area (brightness). Of these but one is essential, the other three following by purely geometrical relations. It is immaterial which of the four is selected as basic and which derived. The maintained standard is one of luminous intensity, establishing the International Candle as a unit, and luminous flux per

[1] E. B. Rosa, Bur. Standards Bull., *6*, pp. 343–373; 1910.

[2] See Report of the Committee on Nomenclature and Standards of the Illuminating Engineering Society for 1921.

unit solid angle as a photometric quantity. The unit, the standard, and the quantity are to be carefully distinguished.

The three other common units follow at once from the international candle, the unit used to measure flux per steradian. Thus luminous flux is measured in lumens, one lumen being the flux within each steradian about an international candle. The factor solid angle, by which the lumen differs from the candle, although of zero dimensions is of vital significance. Flux per unit area is naturally expressed in lumens per square cm. The logical unit of brightness (flux per unit area per unit solid angle) is the candle per square cm (c/cm²) or the lumen per square cm per steradian. One candle per square cm is π lamberts as the lambert has been defined and is being used by illuminating engineers as a unit of brightness.

These four fundamental quantities and units will be used in this paper as above defined, but with broader interpretations than those frequently given them. They will be applied to convergent as well as divergent beams and to points and surfaces in space (e.g., to images) as well as to photometric surfaces. The symbol F will be used for flux in lumens, D for flux per unit area in lumens/cm², C for luminous intensity or candle power and B for brightness in c/cm², as on p. 231 of the 1919 report. The more general interpretation of luminous intensity or candle power is that of flux vergency applicable to convergent as well as divergent pencils. Similarly the quantity brightness, luminous intensity density or candle power per unit area, is generalized in the sense of flux vergency density applicable to incident as well as emergent luminous flux. Unless otherwise specified, the centimeter is the length unit and ω is solid angle in steradians.

The photometric light element is the differential *pencil* of luminous flux. This is the flux wholly contained within an element of solid angle, namely

$$dF = C d\omega$$

where C is luminous intensity as defined above. Such a pencil is specified by intensity, location of apex, and direction of axis. An aggregate of elementary pencils having a common apex is a pencil of light in the ordinary sense (flux and solid angle both finite). In a homogeneous pencil the intensity is the same in every element.

A *zone pencil* is a pencil emanating from a single point of the object viewed or projected and terminating on a given surface or entering the entrance pupil of an optical system. A *field pencil* is a pencil converging from all points of the object viewed or projected, to a point of the sur-

face illuminated or to the first nodal surface of an optical system. A *beam* of light is an aggregate of field and zone pencils both originating and terminating on a common surface. It is therefore a group of rays all of which originate in one given surface and terminate in another. A beam is homogeneous when flux density is constant throughout every cross section.

SIMPLE OPTICAL SYSTEMS

1. LUMINOUS SURFACE. Let the brightness of a luminous surface at any given point in a given direction be $B(c/cm^2)$. Then by definition, $B=dC/dS$, when dC is an intensity element and dS an element of projected surface area, irrespective of the distribution of flux in other directions. Since (by definition)

$$B=\frac{dC}{dS}=\frac{dD}{d\omega}$$

it follows that $dD=Bd\omega$ is the flux in lumens/cm² of projected area emitted within the elementary solid angle $d\omega$ in the direction in which the brightness is B. The flux within a finite solid angle is the integral of that expression.

In case the solid angle is conical of half angle θ, $\omega=2\pi\ (1-\cos\theta)$, and the flux per unit area in lumens/cm² emitted within that angle is therefore the integral of $2\pi B\cos\theta\sin\theta\ d\theta$. When brightness is independent of angle, the value of that integral is $\pi B\sin^2\theta$. Hence in this case the total flux ($\theta=\pi/2$) emitted is $D=\pi B$ lumens per cm² of luminous surface.

The *illumination* produced at a distance d cm in a direction in which the brightness is B c/cm² by a projected element dS of bright surface is $BdS/d^2=B\omega'$ lumens/cm², that is, the flux density in lumens/cm² = the brightness of the luminous surface in c/cm² times the solid angle subtended by that element of surface at the point where the illumination is measured.

2. AN ILLUMINATED SURFACE upon which are incident D lumens per cm² at a given point, emits RD lumens/cm² at that point, R being the reflecting power of the surface. The brightness of a surface so illuminated in any given direction cannot be calculated from its illumination unless the angular distribution of the reemitted radiation be known. In the special case of a perfectly diffusing surface, the brightness B(c/cm²) produced by an illumination of D lumens/cm² is RD/π. In the case of a mirror, plane or curved, the brightness from any point within the beam is that of the source times the reflecting power of the

mirror. Similarly the brightness of a refracting surface, from any point within the beam, is that of the source times the net transmission of the surface.

3. PROJECTED IMAGE. In the formation of an image by a lens or mirror system, the total flux F is the same at every cross section of a small axial projecting beam except for a percentage loss by reflection, absorption, and scatter at the lens or mirror. Hence flux density D varies inversely as the cross section. The luminous intensity or flux vergency dC from each point dS of the object and dC' toward each point dS' of the image is $dC = BdS$ and $dC' = B'dS'$ or $(dD/d\omega)dS$ and $(dD'/d\omega')$ dS'. The brightness or more properly, flux vergency density B is of course such that the transmission T times the flux in lumens in the entering zone pencil is equal to that in the zone pencil leaving the projecting system. Hence

$$\frac{dD'}{dD} = \frac{B'd\omega'}{Bd\omega} = \frac{u^2T}{v^2}$$

u being object distance and v image distance from the apex of the field pencils entering and leaving. Therefore in general the relative flux vergency in object and image is given by

$$B'v^2d\omega' = TBu^2d\omega$$

T being transmission corrected for losses by reflection, absorption, and scatter, by the optical system. This relation is subject to no limitations or assumptions whatever.

In simple optical systems, field and zone pencils are of sensibly equal length and $u^2d\omega = P$ = area of entrance pupil, also $v^2d\omega' = P'$ = area of exit pupil. Hence, in this case

$$B'P' = TBP$$

For the simplest case of a single lens or mirror (*not* for telescopes or microscopes), entrance and exit pupils are of sensibly equal area; $P' = P$ and therefore $B' = TB$, or flux vergency density in an axial direction is the same in the image as in the object if corrected for transmission.

Flux density in the image is from the above

$$dD' = B'd\omega' = \frac{u^2}{v^2}\,TBd\omega$$

due to flux within each elementary solid angle $d\omega$ from the object. If the object beam is homogeneous it follows by integration that

$$D' = \frac{u^2}{v^2}\,TB\omega = TBP/v^2$$

or transmission times brightness of object times area of entrance pupil divided by square of image distance. For a simple lens therefore $D' = TB\omega'$, or flux density in the image = brightness of object, corrected for transmission, times angular aperture of the exit pupil as seen from the image.[3]

4. RETINAL IMAGE. The luminous sensation is determined by the density of luminous flux at the retina, which is related to the brightness of the object viewed, the area of the effective pupil, and certain constants. In this case the lumens/cm^2 at the retina, $D' = BPTn^2/v^2$. The transmission T is roughly 0.95, refractive index n of the vitreous humor = 1.3365 and v the length of image field pencil is 2.07 cm. The effective entrance pupil (the area of which is P cm^2) is the image of the actual pupil formed in front of the eye by the cornea and aqueous humor. Its diameter is 1.14 times the diameter of the actual pupil for an eye focused on a distant object and 1.02 times for an eye focused on an object at 25 cm. Hence for the retinal image (distant object)

$$D' = 0.51\ BP \text{ lumens/cm}^2$$

B being in c/cm^2 or lumens/cm^2/ steradian and P in cm^2 (area of actual pupil).

The above expression for retinal flux density also holds of course when the eye is used as the receiving end of an optical instrument, B referring to the beam entering the eye and P to the pupil area. If the eye and instrument are regarded as a single optical system, P is the entrance pupil of that system. The expression does break down however below the limit of resolving power of the eye and the retina, each being roughly half a minute of arc. The image of an object subtending less than that angle is always spread over a spot or band at least .0022 mm in diameter or width.

5. PHOTOGRAPHIC IMAGE. In photography the problem is one of securing the proper energy density (flux density × time) on the sensitive surface, given a subject of a certain brightness (flux vergency density) in the direction of the lens and a lens of a certain relative aperture. Time of exposure may or may not be limited (about 1/32 second for motion pictures or much less for rapidly moving objects).

[3] In the published treatments of this subject, there exist many ambiguities and misstatements due chiefly to a lack of precisely defined and generally understood fundamental photometric units. The treatment here given is believed to be entirely free from ambiguity. The advantage of a treatment based on flux vergency density (brightness) is obvious. No general relation between flux density in object and image exists but between the flux vergency densities, the relation is simple and free from all assumptions.

The general expression for exposure $E=D't$ in lumen seconds/cm² is

$$E=D't=TBPt/v^2$$

in which T as before is percentage transmission, B is brightness or flux vergency density in c/cm², P is the area of the entrance pupil in cm², t is time in seconds and v (cm) is image distance (not back focal length) measured from the apex of the image field pencil. This expression is limited only by the assumption of homogeneous zone pencils which is a very close assumption indeed for all ordinary photography. As a rough working formula $E=Bt\omega'$ is convenient, ω' being the solid angle subtended by the exit pupil at the image.

Photographic plate and film speeds are ordinarily given in candle-meter-seconds (c.m.s.) but contain an arbitrary numerical factor. 1 lumen/cm² = 10000 lumens/meter² or meter candles. Ordinary negative plates and films require an exposure (E) of roughly .0002 lumen seconds/cm² (=0.2 milliphot seconds) to give unit density (10 per cent transmission) in the developed negative.

6. SCREEN PROJECTION. In pictures projected upon a screen, the photometric problem is to obtain sufficient brightness of picture in the direction of the audience. The brightness of the source (arc crater or incandescent filament) is limited to 2000-5000 c/cm² and with large magnifications is taxed to the utmost to provide the .0001 to .0002 c/cm² minimum screen brightness required for comfortable, accommodated vision.

There are five points of chief interest in projection: (1) the source of light, (2) the condenser, (3) the object plane, (4) the projection lens, and (5) the projection screen. There are eight or more air-glass surfaces causing a loss of about 50 per cent of the light by reflection, scatter, and absorption. In motion picture projection, the shutter cuts off roughly 50 per cent of the remainder. The picture takes between 10 and 90 per cent over most parts of interest and trims off some in the frame. Aside from these losses, the total flux is constant throughout the projecting beam, $F=SD=$constant and $F=BS\omega=$constant. Either formula will serve at any point; flux density inversely proportional to area or brightness inversely proportional to product of area and solid angle. Screen brightness (c/cm²) is of course RD/π, where D is incident flux density in lumens/cm² and R is reflecting power in case the screen surface is perfectly diffusing and either more or less for other surfaces depending upon matness and the angle from which it is viewed. No projection apparatus can give a greater total beam flux at any

point (e.g. on the screen) than that at the source in the direction of the condenser, improvements merely minimize losses.

7. SCREEN TESTING. Screens have been made which produce almost every conceivable variety and degree of diffusion in either reflected or transmitted light. The reflection (or transmission) ranges from purely specular to purely diffuse and may be either symmetrical or unsymmetrical about either an axis or a plane. Tests give brightness as a function of angle under a given illumination. From brightness the flux may be computed and then integrated (graphically) to give total flux and reflecting power or transmissivity.

Suppose a screen to be illuminated at a given angle θ_0 with the normal by a small spot of light S_0 cm^2 in area and L cm away, whose brightness is B_0 c/cm^2 in that direction. The illumination produced at the screen is B_0S_0/L_0^2 lumens/cm^2. B_0S_0/L_0^2 may be written $B_0d\omega_0$, $d\omega_0$ being the solid angle subtended at the screen by the source of light. In tests of one important class of screens, $S_0=100\text{cm}^2$, $L_0=100$ cm, $d\omega_0=0.01$ steradian and $\theta_0=0$ is standard.

Let the brightness B of the illuminated screen under test be determined at various angles θ from the normal. The values obtained will lie between two extremes: (a) when reflection (or transmission) is purely specular, the brightness B observed is $B=RB_0$ (or TB_0) at the angle $\theta=\theta_0$ and $B=0$ at all other angles. (b) When the reflection (or transmission) is perfectly diffuse, the observed brightness is $B=RB_0\cos\theta_0d\omega_0/\pi$ (or $TB_0\cos\theta_0d\omega_0/\pi$) whatever the angle of observation θ. With a moderate angle of illumination ($\omega_0=0.01$, say) specular brightness may be several hundred times diffuse brightness.

The general problem is to determine the distribution and amount of the reflected (or transmitted) light from the brightness curves. If at any angle θ the observed brightness is B c/cm^2 of projected area, the flux in that direction is $Bd\omega$ lumens/cm^2 of projected area of illuminated surface within each element of solid angle $d\omega$. The flux from each square cm of actual surface is $Bd\omega\cos\theta$ lumens. This can be integrated only graphically unless B is expressible as an integrable function of θ. Graphical integration may be readily performed if sufficient data is available. Two special cases, covering nearly all practical testing, will be discussed.

In the special case of nearly normal illumination (such that $\cos\theta_0=1.00$) and axial symmetry of reflected or transmitted light, $d\omega$ may be taken as a differential conical shell making an angle θ with the axis (of

illumination and of symmetry). In this case $d\omega = 2\pi \sin\theta\, d\theta$ and hence the flux (in lumens) within that conical element is

$$Bd\omega \cos\theta = 2\pi B \cos\theta \sin\theta\, d\theta$$

For graphical integration, B is plotted as a function of θ, then each ordinate of this curve is multiplied by $2\pi \cos\theta \sin\theta$ and replotted. The area of the second curve is the total flux reemitted by the screen. Reflecting power (or transmissivity) is the ratio of this integrated flux to the incident flux.

Another case of considerable interest is that of symmetry about two planes perpendicular to each other and to the screen illuminated (ribbed or corrugated surface). Brightness readings are taken at various angles θ in one plane of symmetry and ϕ in the other. In this case the elementary solid angle $d\omega$ in the expression $Bd\omega \cos\theta$ (or $\cos\phi$) for the outward flux, is to be taken as a narrow pyramid, $d\omega = d\theta\, d\phi$. The two brightness curves (taken in planes at right angles to each other) are plotted as functions of angle. The brightnesses taken in the θ plane are multiplied by $\cos\theta\, d\theta d$ and replotted thus giving the flux within the solid angle $d\theta\, d\phi$ as a function of θ. Flux as a function of ϕ is obtained in the same manner. The solid integral of the two curves gives the total flux remitted.

Relatively very few cases do not fall in one or the other of the two classes above discussed and most of these may be handled by similar methods.

SCHENECTADY, NEW YORK

Quantity of Light Energy Required to Render Developable a Grain of Silver Bromide. [*A Correction.*]—Attention should be called to several mistakes which are found in an article with the above title in the December, (1922) number of this Journal, pp. 998–1015.

The width of the slit-opening of the monochromator should be given as 1.5 mm$\times$20 mm, instead of 4 mm$\times$20 mm; and the dispersive power of the instrument should be stated as 150 mm/μ, instead of 56 mm/μ.

In the table of "Experimental Results," the heading "Light Energy in Quanta (at 0.549μ) per mm," should be changed to "Light Energy in Quanta (at 0.549μ) per mm$^2\times 10^{-7}$," and the caption "Quanta (at 0.549μ) per Grain" should read "Quanta (at 0.549μ) per Grain $\times 10^{-7}$." The paper should conclude with the statement that "...about 2.3 $\times 10^7$ quanta of incident light of mean wave length 0.549μ are necessary to render developable a grain of silver bromide."

P. S. HELMICK

THE D_2 ZEEMAN PATTERN FOR RESONANCE RADIATION

By Paul D. Foote, A. E. Ruark and F. L. Mohler

The Sommerfeld-Landé interpretation of the anomalous Zeeman effect[1] shows how the complicated patterns may be explained as due to alterations in the atomic energy levels associated with the various spectral series terms. Thus the 1*s* level for an alkali is changed by the magnetic field into two levels differing from the normal state by the energy $\pm h\Delta\nu_{\text{norm}}$ where $\Delta\nu_{\text{norm}} = \frac{e}{m}\frac{H}{4\pi c}$ is the characteristic displacement in the normal Zeeman effect. The $2p_1$ level is changed by the field into four levels differing in energy from that of the normal $2p_1$ state by $\pm 2h\Delta\nu_{\text{norm}}$ and $\pm \frac{2}{3}h\Delta\nu_{\text{norm}}$.

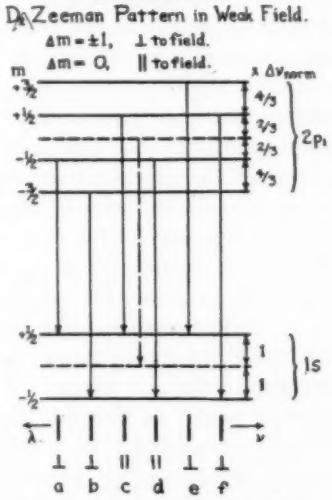

FIG. 1. *Zeeman pattern for D_2.*

These levels are represented graphically by the horizontal lines in the energy diagram of Fig. 1. The numbers at the left show the magnetic quantum number *m* characterizing each level.

[1] Somerfeld, Atombau; ZS. f. Physik, *8*, pp. 257–72; 1922. Sommerfeld and Heisenberg, idem *11*, pp. 131–54; 1922.

Sommerfeld and Heisenberg[2] have derived a selection principle (an extension of the empirical selection principle of Landé) which shows that only those interorbital transitions are possible for which $\Delta m = \pm 1$ or 0. When $\Delta m = \pm 1$ the resulting lines are linearly polarized perpendicular to the field in the transverse effect and when $\Delta m = 0$ the linear polarization is parallel to the field. The possible transitions in accordance with this conception are shown by the vertical arrows in Fig. 1. In the lower part of the diagram the resulting Zeeman pattern for D_2, $\nu = 1s - 2p_1$, is plotted on a linear scale of wave numbers. The line splits into a sextuplet, the two inner components vibrating parallel to the field and each group of two outer components vibrating perpendicular to the field.

The object of the present note is to point out a rather curious deduction which follows from the above quantum-theoretical interpretation of the phenomenon.

Suppose that a bulb of sodium vapor at very low pressure is placed in a uniform magnetic field. Each atom assumes one of the two states $1s \pm \Delta\nu_{\text{norm}}$ and each state is present in the same concentration. Let the vapor be illuminated, normal to the lines of force, by a beam of radiation, having a spectral width at least equal to *af* and linearly polarized with the electric vector parallel to the field. The atoms are therefore capable of absorbing only the components *c* and *d*. Following the absorption, certain atoms exist temporarily in the states $2p_1 \pm \frac{2}{3}\Delta\nu_{\text{norm}}$ but no atoms will be found in the states $2p_1 \pm 2\Delta\nu_{\text{norm}}$, corresponding to the two outer levels of the $2p_1$ group. The excited atoms so formed then return to the $1s \pm \Delta\nu_{\text{norm}}$ states by the four transitions illustrated, giving rise in the resonance radiation to the components *a*, *c*, *d*, and *f*. The components *b* and *e* should be absent since they originate in the states $2p_1 \pm 2\Delta\nu_{\text{norm}}$ which can not be produced under the conditions of the experiment.

At first consideration it might be thought that the energy of the $2p_1 \pm \frac{2}{3}\Delta\nu_{\text{norm}}$ states could be modified by temperature so that the highest and lowest energy levels would be present, as follows from the Nernst reaction isochore.[3] However, it must be remembered that all of the $2p$ states are of exceedingly short life, probably of the order 10^{-8} seconds, so that the statistical equilibrium necessary for the thermodynamical relations by no means obtains.

[2] Loc. cit.

[3] Cf. "Origin of Spectra," Foote and Mohler, Chapter VII.

We may therefore draw the interesting conclusion that the Zeeman pattern for the resonance radiation under the conditions postulated should be a quadruplet instead of a sextuplet. Furthermore, although the original exciting radiation was polarized parallel to the field, the emitted radiation, as viewed in the transverse effect, should have two components polarized with the field and two polarized at right angles to the field. The latter arise in the light which is circularly polarized in the longitudinal effect.

On the classical theory there is no difficulty in conceiving of the resolution of linearly polarized light into opposite, circularly polarized components, the axes of which are parallel to the direction of propagation of the original beam. Here however, the electric vector in the original beam vibrates parallel to the axis of the circular polarization. Although the original light is plane polarized and hence can communicate no moment of momentum to the atom, still the atom as a result of the absorption of this radiation is enabled to emit circularly polarized light possessing angular momentum. The source of this angular momentum is the magnetic field.

A similar analysis may be carried out for other resonance lines. Excitation parallel to the field should produce all four components of the D_1 pattern. The resonance lines of the alkaline earths give rise to no peculiarity. The lines $2p_2-2s$ and $2p_1-2s$ of thallium, etc., should behave like D_1 and D_2 respectively. In the pattern for $2p_2-3d_2$ the two outer components should not appear while $2p_1-3d_2$ should give the entire pattern. In the pattern for $2p_1-3d_1$ the two components possessing the normal separation should be absent.

It is evident from the above that a study of the Zeeman effect for resonance radiation has interesting possibilities.

BUREAU OF STANDARDS,
WASHINGTON.

Spectrophotoelectrical Sensitivity of Bournonite and Pyrargyrite.—The present paper, considered in connection with previously published data on proustite (Bureau of Standards Scientific Paper, No. 412), represents a study of the effect of chemical constitution upon spectrophotoelectrical sensitivity.

Experimental data are given on the effect of temperature and of the intensity of the radiation stimulus upon the photoelectrical sensitivity of the minerals bournonite and pyrargyrite, in the spectral region extending from 0.3μ in the ultraviolet to 2μ in the infrared.

The spectrophotoelectrical reaction curve of bournonite is entirely different from that of the constituent sulphides of copper and lead

(which are not photo-sensitive) and of antimony which has its photoelectrical sensitivity confined principally to a band at 0.77μ in the extreme red. On the other hand, bournonite has a high spectrophotoelectrical sensitivity extending from the extreme violet to 1μ in the infrared, with two wide, ill-defined maxima in the region of 0.55μ and 0.95μ respectively.

On lowering the temperature the intrinsic spectrophotoelectrical sensitivity of bournonite is greatly increased and the maxima shift towards the short wave lengths. The maximum in the violet usually remains the more intense at the lowest temperatures.

The spectrophotoelectrical reaction of the mineral pyrargurite, which is a double sulphide of silver and antimony, is entirely different from that of the constituent sulphides of silver and of antimony, which also exhibit photosensitivity.

At 22°C the photoelectrical reaction of pyrargyrite consists of a wide unsymmetrical maximum in the ultraviolet, with a weak, ill-defined maximum in the region of 0.63μ.

At low temperatures, −165°C, pyrargyrite reacts electrically to radiations of all wave lengths extending from the extreme ultraviolet to 1.5μ in the infrared; but the greatest photoelectrical reaction is localized in the band at 0.63μ.

There is a great similarity in the spectrophotoelectrical and chemical properties of pyrargyrite (silver-antimony sulphide) and of proustite (silver-arsenic sulphide). In a general way the foregoing properties of photoelectrical reaction spectra are analagous to properties of absorption spectra, as affected by chemical constitution, from which it appears that perhaps ultimately the two phenomena may be traced to a common source within the molecule. [W. W. Coblentz, Bureau of Standards Scientific Paper No. 451.]

Overtones in Infrared Absorption Spectra.—Measurements on the transmission of the gases CO, HCl, and HI, and the crystalline solids $SrSO_4$, SiC, $CaCO_3$, and a mineral sulphate called "Langbeinit," in the wave length range $1–20\mu$, supplemented by measurements on the reflecting power of the crystals; all with the object of finding whether the absorption frequencies for each substance could be classified into fundamentals and multiples of these by 2, 3, and other small integers. A strong band and its octave were observed in each case except $CaCO_3$; in several cases the second harmonic overtone, and in one—that of $SrSO_4$—the fundamental and the first three overtones. The spectrum of $CaCO_3$ was too intricate to be interpreted. Either the best sets of data are not always reproduced or else some of the absorption frequencies are identified from very inconspicuous irregularities on the curves. [C. Schaefer and M. Thomas. (Marburg.) ZS. f. Physik, *12*, pp. 330–341; 1923.]

KARL K. DARROW

ON THE MEASUREMENT OF STANDARD WAVE LENGTHS

By Keivin Burns

The historical development of spectroscopy, leading up to the determination of standard wave lengths, has been so thoroughly and so clearly treated by Kayser[1] that it would be unwise to discuss it in an article restricted in length as the present one necessarily must be. The subject has been brought up to date by Meggers[2] and all who plan to undertake the determination of accurate wave lengths should become familiar with these references and the others listed on page 436.

The present situation is briefly as follows: The standard meter has been compared with the wave length of the red cadmium line by Michelson[3] and by Benoit, Fabry and Perot,[4] the resulting accepted wave length being 6438.4696A. The value of the angstrom (A) was settled in this way. (Hereafter wave length is abbreviated λ, the plural being λλ). Various observers have compared this cadmium λ with the λλ emitted by the iron arc, by the inert gases, and by cadmium. In the region 3370–6750A three observers have compared the *Fe* spectrum with the fundamental λ and a fairly satisfactory system of secondary standards[5] exists in this part of the spectrum. For λλ shorter than 3370A and longer than 6750A, one or more series of observations connect the spectra of *Fe*,[6] the inert gases,[7] and of *Cd*,[7] with the fundamental standard λ, but no λ shorter than 2375A nor longer than 8950A has been compared directly with the fundamental. And in the *Fe* spectrum, those λλ greater than 6750A are not entirely satisfactory. Tertiary standards[8] have been derived, from an intercomparison of the *Fe* lines, at close intervals throughout the region for which satisfactory secondary *Fe* standards are available, (3370–5500 and 6000–6750A).[8E]

It is seen that the greater portion of the range of spectrum that can be photographed contains no accurately determined standards. This fact should stimulate spectroscopists to take up this work which is of such vital importance in all spectroscopic lines, and particularly in connection with atomic theory. The determination of accurate λλ is beset with difficulties no more trying than in the case of any other careful investigation. The labor of observing and measuring is tedious, but the investigator is repaid by results of fundamental and lasting importance. The constant differences observed in the spectra of *Ne*,

[1] Citations are given at end of article.

A, and *Cd*, show an accuracy of a part in several million, and one is readily fascinated by the high degree of precision which is possible in this class of work.

SOURCES

Certain conditions must be fulfilled by λλ which are to serve as standards. The first essential is reproducibility, which implies that the λ will be the same in any laboratory and that it can be measured with the greatest precision. Further, the source should be one that can be, and will be, generally used. It is evident that only sharp lines can serve as standards. An observer usually wishes to cover a considerable range of λλ at one time, therefore the source of standards should furnish lines throughout as great an extent of spectrum as possible. The *Fe* arc, recommended by the American Committee,[9] satisfies these conditions in a high degree throughout the regions 2400–5500 and 6000 A. The vacuum arc furnishes sharper lines, but the additional inconvenience of maintaining a vacuum seems to have prevented the general use of this source. The inert gas spectra are perfect in the regions in which their lines occur, but each one leaves considerable gaps in the part of the spectrum most frequently photographed. The gases *Xe* and *Kr* are not easily available at present, but *He*, *Ne*, and *A* are readily obtained. On account of the sharpness of their lines, and the intensity of spectrum that may be obtained, these spectra should be fully investigated by several observers, comparing the λλ directly with the fundamental standard. The absorption lines of iodine[6E] give promise of becoming very accurate and convenient standards, and the telluric absorption lines in the solar spectrum deserve far greater attention than they have as yet received.[10]

It is not possible to define a wave length independently of the conditions accompanying its production: Lack of space prevents a full treatment of this very complicated matter. The precautions advised in the following paragraphs are intended to put the observer on guard, so that any difference in wave length found between two series of observations may be assigned to the proper cause. It is worth noting that in general sharp lines are less affected than are broad ones by changes of conditions in the source.

In observing λλ for purposes other than to serve as standards the conditions necessarily must depend upon the nature of the investigation, yet all conditions should be carefully noted. In case of a metallic arc[25] or spark, open or in vacuum, one should record the size and shape

of the electrodes, the length of the arc and the part observed, also the voltage, current density, and the pressure of each component of the surrounding gas. If the electrodes consist of a mixture of elements, the proportion of each and its behavior should be noted. The use of capacity, inductance, auxilliary spark gaps etc. should be recorded, and in the case of a vacuum tube, the size and shape of the tube. In any work the temperature of the electrodes may be of importance. In vacuum tubes fed by direct current it is conceivable that the Doppler effect might influence the wave length. Even if a.c. is used, the tubes often rectify to some extent. It is therefor advisable to set the axis of the capillary perpendicular to the axis of the collimator, although in practice no effect of this nature has as yet been found in connection with the use of ordinary vacuum tubes, even of the end-on H-type.

The observed λ will be a function of the temperature and pressure of the air in the neighborhood of the principal dispersive agent, whether interferometer or grating.

PRIMARY STANDARDS

The first system of accurate primary standards was determined by Bell[11] who used plane gratings ruled on glass. While this method has been superceded by the use of the interferometer, the latter cannot be used with facility in all parts of the spectrum and the grating is still being employed for measuring wave lengths in much the same manner as if fundamental standards were being determined. It may therefor be useful to review the requirements for such work. It is obvious that the temperature of the whole apparatus must be kept constant, and must be accurately known. The grating space, as it is actually used, must be evaluated in terms of the fundamental standard of length with the same degree of precision as that of the observed λ. The angles of incidence and emergence must be measured with the highest accuracy. It is doubtful whether an accuracy greater than a part in a million can be obtained in this type of measurement. The limit will usually be set by the accuracy of the measured angles, and the experience of astronomers has shown that it requires a great deal of effort under the most favorable circumstances, to measure an angle to one part in 200 000. These considerations lead to the use of some other method of determining fundamental and secondary standards.

The method used by Michelson[3] to determine the fundamental wave length appears to be capable of obtaining results with an accuracy of one part in a million or better. The number of waves was counted in

a length of 0.65 mm and then a second standard twice as long as the first was compared with twice the length of the first. In this manner a standard of 10 cm length was evaluated in terms of the three strong *Cd* lines, and finally the prototype meter was evaluated in wave lengths by displacing the 10 cm standard ten times. As compared with the grating, the interferometer offers the advantages of directness, and of greater ease in controlling and knowing the temperature.

A simpler, and perhaps more accurate method, was introduced by Benoit, Perot, and Fabry.[4] End standards are carefully adjusted to the lengths 100, 50, 25, 12.5, and 6.25 cm. These are of invar, which has a small coefficient of thermal expansion. The standards are essentially sets of three pins which separate plane silvered glass surfaces. The parallelism of the plates on the two ends of each standard is adjusted by means of multiple reflection, and this may be done with a degree of accuracy beyond the requirements of the problem. Each standard is compared with the next longer by means of white light fringes, and the difference between the longer and twice the shorter is accurately determined by rotating one of the standards. The angle of rotation need be known only to a fraction of a degree. Finally, the number of waves in the length of the smallest standard is determined by photographing the interference rings of the *Cd* lines, the whole number being found by fractional differences. The whole operation is completed in an hour or two, insuring constancy of conditions. The λ of the red *Cd* line so obtained has an accuracy of one part in 5 or 10 million, the determinations by Michelson and by Benoit, Perot, and Fabry being in almost exact agreement.

Further determinations of the Fundamental standard of wave length should be undertaken only after international conference.

SECONDARY STANDARDS

The grating as an instrument for determining secondary standards has been largely, if not entirely, superseded by the interferometer. The grating method is treated under "Tertiary Standards." The various types of interferometer are well suited to this work, the Fabry and Perot type[6A] being the one in most general use. This consists essentially of two plane plates separated by three pins of equal length. The used faces of the plates are coated with a semi-transparent metallic film and the plane of the unused face subtends a small angle with the used side in order to avoid overlapping ring systems.

The separators may be of any material if the instrument is to be used at constant temperature. They are often made of invar, because of its small coefficient of thermal expansion. However, the change of the elastic properties of invar with temperature renders it not much superior to steel or brass, since it is necessary to use a certain amount of pressure in adjusting the plates to the rods. Fused silica recommends itself for separators. This material may be obtained in the form of tubes of suitable dimensions, and it is fairly simple to fashion a separator by sawing and grinding. It is advisable to have separators ranging from 2 mm to 50 mm. For special work in the extreme ultraviolet shorter separators may be necessary and these may be specially made. A bent platinum wire of proper diameter has been used to advantage. The length of the separators is measured by means of a micrometer caliper, and the exact order of some standard line is found by observing the wave lengths in a known spectrum,[4] such as *He* or *A*. For this purpose it is best to use two lines of nearly the same wave length, and two others that differ in wave length, as much as is convenient, from these two and from each other. For separators of 40 or 50 mm length, the wave lengths must be accurate, or the wrong order may fit all four lines within the error of the wave lengths. Three trials are usually sufficient to find the correct fractions, even though the preliminary measurement of the separator is in error by several microns.

The choice of material for the reflecting surfaces is regulated by the region to be observed.[12] For a part of the spectrum a thin film of chemically deposited silver suffices. In general, however, it is better to make all reflecting surfaces by cathodic deposition. For the region 5800 to 9000A copper is excellent; between 3500 and 7500A silver is good; platinum is useful from 2800 to 7500A; nickel is unsurpassed for use from 2300 to 3500 and gives the best surface for comparing the region 2300–2800A with the fundamental standard. For λλ shorter than 2200A aluminum or silicon can be used; both are difficult to deposit uniformly on quartz. Professor Pfund reports that unsilvered plates give fair fringes in the ultraviolet, and more recently Fabry suggests the use of unsilvered plates of fluorite in the extreme ultraviolet. Using unsilvered plates, the minima, not the maxima, of the fringes are measured. As yet no λλ have been measured by means of unsilvered plates. By means of metallic films it has been impossible to obtain fringes for any but the most powerful lines of λ less than 2200A. Quartz plates are used for λλ shorter than 3600A but there is

no gain in using quartz with silver or copper, as the reflecting power of these metals is very low in the region to which glass is opaque. The plates of quartz are made of equal thickness, one being right handed, the other left.

To separate the lines of the spectrum an auxiliary spectrograph is usually necessary. A concave grating, mounted in parallel light, is very useful for this purpose; a plane grating with properly chosen lenses may be even better. When the spectrum under observation has but few lines, all well separated, a prismatic spectrograph may have sufficient resolution, and greater intensity, while being more compact. The defining power of the spectroscope is sufficient if a point on the slit is rendered by a point in the image, or by a sharp line at right angles to the slit. For red and infrared work a grating is preferable; in the region 4200–6700A any spectroscope of moderate power will serve for most spectra; for the ultraviolet a quartz instrument is to be preferred to a grating on account of the greater intensity obtainable. Yet a grating may be used for arc spectra as far as 2300A. A spectroscope having optical parts of quartz and fluorite, or quartz and rock salt,[7D] is convenient for ultraviolet work.

To project the images of the rings upon the slit a telescope is required which is achromatic over the whole range of spectrum under observation. This condition is fulfilled for the region 2500–8000A by a quartz-fluorite lens. A system of mirrors gives perfect achromatism for all wave lengths and is to be recommended for general use. For the very short waves, 2000–2300A, magnalium is a better reflector than speculum. Concerning the range of spectrum to which a given metal is suited, the remarks made in connection with interferometer mirrors apply also to auxiliary mirrors. Yet the latter, being thick, have greater reflecting power than the films, which must be semi-transparent, and speculum is a fair reflector throughout the whole range of spectrum that can be observed by interference methods.

REPÉRE.—In primary and secondary work it is necessary to know the scale of the ring system. This requires that the equivalent focal length of the telescope, which projects the rings on the slit, shall be known; and this telescope must be adjusted with precision. The ratio of the scale of the ring system, as measured, to the scale at the slit is also required. For tertiary work, or for interpolation of any sort, these data may be derived in a simple manner from the diameters of known lines,[8D] and the gauge at the slit may be used or dispensed with, according as the one or the other procedure seems to be the more con-

venient. As a *repère*, or gauge, the writer prefers a system of narrow slots perpendicular to the slit and placed almost in contact with the same. By photographing the light that passes through this gauge, the scale at the slit and on the plate can be compared. The angular scale of the rings must be derived from the constants of the projection telescope. The required constants are: The back focus; the axial equivalent focal length; the distortion over the range of the angular size of the rings which are to be used. These data may be observed by any of the methods used in lens testing.

RING MEASUREMENT.—Interference rings are sharp on the outside and shade toward the center of the system. This condition limits the accuracy obtainable in measuring, and bears on the choice of rings for measurement. The dispersion is greatest in the innermost ring and becomes rapidly less with increasing ring number. However, because of the shading, it is wise to avoid the innermost ring unless its fractional order is over 0.4. The best results are obtained from a ring of such an order that the next smaller shows only a trace. There is little to be gained by measuring more than two rings. Any sort of measuring device will do for the measurement of the rings, as the accuracy required is only of the order of 0.02 mm.

CERTAIN SOURCES OF ERROR.—The reader should be familiar with references 6 and 2 which give the development of the formulas needed in interference measurements of the type under discussion. It is readily deduced from these formulas that the diameter of a ring of any given fractional order is proportional to the square root of the wave length. By fractional order is meant that quantity which must be added to the order of the ring to make it equal to the order of the center of the ring system of the wave length in question. Suppose 8000A has the order number 1000.5 and a line in the neighborhood of 2000A has the order number 4000.5, the fractional order of the first ring will be 0.5 in each case and the diameter of the ring of less wave length will be just half that of the ring of greater wave length. It is customary to throw an image of the source upon the interferometer. Each point in the ring system arises therefore in a definite part of the source. And to a certain extent each ring is due to a definite part of the interferometer. Remembering what has just been said of the variation in size of rings with wave length, it is seen that errors in comparing one line with another may arise through aberrations in the lens (or mirror) system, and through irregularities in the figure of the plates or in the uniformity of the films. Even when observing lines of nearly the same λ

the first ring of one may be of fractional order 0.5, followed by 1.5, 2.5 etc., while another line may have the orders 0.0, 1.0, etc. In such a case the two ring systems will be affected differently by aberrations and irregularities such as have just been mentioned. Whenever standards are found throughout the region under investigation, as when tertiary standards are being interpolated between secondaries, the effects of these errors can be eliminated as follows. After taking two photographs of the region, the interferometer plates are rotated 45° in opposite directions and the length of path is changed by a fraction of a wave. Two more exposures are made, and the rotating and change of length repeated. One may thus observe a given line with the first ring of order 0.6, 0.9, and 1.2. For this reason the use of separators of quite different lengths is to be recommended, as well to be able to separate very close lines which might be in phase at any particular difference of path. If possible, two or more pairs of plates should be used in each investigation.

The ring system must be accurately centered on the slit, as any lack of centering will affect the large and small rings by different amounts. If the source under observation is faint or invisible, some source of intense rings must be used in adjusting. The mercury lamp is a source of intense sharp lines; this and a right angle prism back of the slit are useful adjuncts of the spectrograph.

In secondary work, where the line to be observed is usually of very different wave length from that of the fundamental standard, the tactics outlined in the preceding paragraphs are useful but do not suffice. In such work it is advisable to use an accurate repére, as previously described. It should be possible, if necessary, to determine the scale of the plate from a pair of apertures separated by about the diameter of any particular ring.

PHASE CHANGE.—There seems to be some misconception regarding the bad effects of dispersion of phase in interferometric measurements. It is obvious that whenever there are standards throughout the region under investigation there can be no question of phase change. It is completely eliminated by using the correction curve obtained by plotting the observed values of the standard lines against the accepted values. And in secondary work the phase change is completely eliminated by the use of interferometers of different thickness. In the latter case we have a difficulty similar to that treated above; the ring systems vary in size with the length of path. The elimination of the effects of phase change reduces itself to the overcoming of errors due

to aberrations and to irregularities. It is to be noted that the effects of phase change and other errors decrease with increasing order number.

A convenient method of eliminating the effects of all these errors consists in plotting the $\lambda\lambda$ for several or all of the lines under discussion as actually determined by interferometers giving orders of 5 000, 10 000, 20 000 etc. up to the highest order that can be observed. These $\lambda\lambda$ plotted against the order (or better, the reciprocal length of path) furnish a curve for each line clearly indicating the λ that would result from an interferometer of infinite thickness which would be unaffected by phase change and other errors. It is well to use not less than three nor more than five interferometers for any particular region. One of these should give a low order, one an intermediate, and the others should give orders about as high as the various lines in question will stand. The formation of the curves for the elimination of phase change, and these are usually straight lines, afford a simple method of applying the weights to be assigned to the mean results derived by means of each interferometer. The correction for phase so determined may be used to correct later observations, yet it is well to note that this correction sometimes changes rapidly in the case of freshly deposited films. It may even change after years, through crystalization or through chemical action. One should therefore always observe in such a manner that the phase change can be eliminated or evaluated.

The temperature and pressure of the air within the interferometer must be recorded in primary and secondary work, and in primary work humidity and CO_2 content of the air must be known. When interpolating, the condition of the atmosphere has no effect on the observed wave length, but the data should be noted. For the region 2 000-10 000A the Bureau of Standards Refraction Tables[14] furnish the means of reducing the wave lengths to normal. It is wise to work as nearly as convenient under standard conditions ($15°C$, $76cm\ Hg$), but far more important to have constant conditions. The temperature of the interferometer may very easily be kept constant to 0.5°, and this should be done.

Whenever possible simultaneous exposures should be made on the standard and the unknown. This may be done by imaging one source upon the other, both being in line with the axis of the collimator of the spectrograph. Or one source may be imaged upon the interferometer by the aid of a lightly "silvered" mirror through which the other source shines directly. If simultaneous exposures cannot be made, the standard should be observed both before and after the unknown, and if at

all convenient the exposure on the unknown should be interrupted one or more times to expose the standard.

As mentioned in the, foregoing, very close companions to spectral lines may be observed by means of the *F* and *P* interferometer by the proper choice of difference of path. It will seldom happen that all the close lines in a given region can be observed by a single path length. For close lines, and particularly in observing the Zeeman Effect, the echelon grating and the Lummer-Gehrcke plate are valuable dispersive agents. It is to be noted that text books indicate that the auxiliary prism is put in the beam of light before the echelon. In photographing, this auxiliary prism or grating should ordinarily be placed after the echelon, thus permitting a long range of spectrum to be observed in one adjustment of the apparatus.

It is obvious that the standard and unknown region must both be accommodated by the spectrograph. The fundamental standard is not very brilliant, and yet, to minimize deterioration of the tubes, a short exposure on this standard is advisable. It is often preferable to use separate cameras for standard and unknown, the slit being in common. A red screen over the cadmium lamp allows only the fundamental line to pass, and this may be photographed by a simple camera immediately back of the slit, a removable mirror or prism being used to give the beam the proper direction. This arrangement precludes simultaneous exposure. If a prism spectrograph is used to separate the lines of the unknown spectrum, the *Cd* line can be photographed through the prism. If the observed region is of much shorter λ than the standard, an auxiliary lens may be used to shorten the *Cd* exposure without preventing simultaneity of exposure. If the dispersive element is a plane grating an auxiliary lens for the *Cd* can frequently be used in connection with an order that is not used for the unknown.

If a standard other than the primary is used, it will be chosen for greater brilliance and convenience and the proper method of obtaining simultaneity of exposure will suggest itself; in fact, that consideration will have great weight in determining the choice of the auxiliary standard. As auxiliary the following are suggested, the choice to be governed by the conditions of the particular problem: The secondary Iron standards;[5] Cadmium;[7D] the inert gases, especially Neon.[7B]

TERTIARY STANDARDS

Tertiary standards may be observed in the same manner as secondary standards, already discussed. But the term "tertiary" implies that

Secondary standards are available, and these being distributed throughout a considerable range of spectrum, the problem of determining tertiaries is greatly simplified. The measurement of λλ for most other purposes will follow the course to be pursued in this connection. The grating can be used to advantage in tertiary work, whenever values are to be interpolated between standards, and when an unknown region may be compared with known lines in an overlapping order. The question has often been raised as to whether the second order gives λλ exactly half the values in the overlapping first order. Perhaps some gratings are faulty in this respect, but probably any grating which gives theoretical resolution, when in perfect adjustment, renders the overlapping orders correctly. Some supposed errors may have been due to insufficient attention to atmospheric dispersion, and to details about to be mentioned.

In observing an extent of spectrum amounting to, say, 1500A, on plates which accommodate only 500A, the whole region might be covered by three adjustments: Yet it is better to use five, so that the short wave half of one region becomes the long wave half of the plate in the next adjustment. Similarly, in measuring if the plate is longer than the screw of the comparator, the plate should be so adjusted on the instrument that a part of the lines first measured can be observed with the next section. Then the whole region of spectrum should be tied together by plotting all the sharp lines. If only the standards are used for plotting, the points are sometimes too few, and no account can be taken of errors in the values or in the measurements of standards near one end of the run of the screw. In measuring two plates of the same region with a screw shorter than the plate, the break in the measurement should come at a different part of each plate. Observing these precautions, 2000A of spectrum can be measured by means of a comparator accommodating only 130A, without introducting any error due to the inaccuracy of standards 50A apart.

In comparing two regions of spectrum by means of a grating, or when comparing two sources in the same region, it is vital that the radiation in both cases pursue *identical* paths in the instrument. If the exposures cannot be simultaneous, the effective exposures of the two sources should coincide in time. This is not important if the exposures are very short, or if the whole apparatus is free from vibration and temperature effects, conditions difficult to realize. If it is necessary that light from one source pass through one part of the slit and light from the other source through another part, these conditions must be

reversed for half the observations in a series. For it is possible to measure the mean of a number of fairly sharp lines, such as the *Fe* spectrum, with an accuracy in excess of the degree of straightness of most slits. Further, the lines in grating spectra are usually curved,[15] and the dispersion corresponding to the ends of the slit is in general different from that corresponding to the middle point thereof. This curvature is not a large quantity but it is usually measurable in all prism and grating spectra.

Whether a grating or an interferometer is to be preferred for interpolating must depend on the character of the spectrum to be investigated. Where the highest accuracy is of importance, one should use both instruments if they are available. It is a mistake to think that the measurement of λλ by means of the interferometer is more laborious than observation by means of a grating, for the reverse is often the case.

While extrapolating cannot be done with great accuracy by means of a grating, there is no better means at present for measuring the λλ shorter than 1000A. By means of multiple slits, Lyman[16] has covered the Schuman region with an accuracy of 0.5A. Millikan, Bowen and Sawyer[17] use the zero order and several higher orders to compute a formula by which the very shortest λλ may be derived. These observers take into account the position and shape of the photographic plate, as well as the grating constants. A purely empirical curve may be more simply derived with no great loss in accuracy.

INTENSITY EQUATION.—Comparing Burns's *Fe* λλ with Rowland's Solar Table in the region near 4000A, it is seen that the two series differ by an amount which varies with the intensity of the line. This may arise from the difference in conditions in the two sources, or from the circumstance that we are dealing in the one case with absorption, and in the other, with emission. Yet the same type of difference is sometimes encountered in comparing plates of the same source, taken close together in time, with the same instrument, and it is found in comparing the published work of different observers. When due to purely instrumental causes it may arise from an irregular change in temperature, or it may be due to slight maladjustments of the instrument. In order to avoid this difficulty it is of prime importance that the grating be so adjusted that the secondary maxima on either side of a sharp line are of equal intensity. It is to be noted that a grating may show very good definition even when this condition is not at all fulfilled. It is reassuring to find by an examination of the values recently published

by St. John and Babcock[8D] that an intensity equation can be completely avoided. On account of the nature of the rings, it would seem that the interferometer might be particuarly subject to this type of error, yet it is found that such is not the case.

SPECTROGRAPHS

PRISMATIC.—In the determination of accurate λλ the prismatic instrument is far more likely to be used as an auxiliary rather than as the principal dispersive medium. The reader is already familiar with some text dealing with the design and adjustment of prism spectroscopes, yet he is advised to peruse Kayser and Baly.[18] A point which is too little emphasized in all texts is this: The spectroscope should be designed or arranged for the particular problem and should be as simple as possible under the conditions so imposed. The mounting should be rigid and the prism held firmly but without strain. The necessary adjustments are described in all texts; yet it is worthy of note that the most important part of any region under investigation may profitably be observed near the axis of the camera with M. D. set for it.

As to optical material: Glass may be used for the region 3600–9000A; quartz is transparent to waves longer than 1800A; fluorite transmits the Schumann region; but no substance is very transparent to waves shorter than 1300A.

For the camera, a four piece lens can be designed to have a long range of achromatism and a large flat field. The quartz-fluorite lens, used in observing the ultraviolet, gives good achromatism but to date has not been made in the four piece form, which might be done with resulting increase of field. A simple telescope lens, suitably corrected for color, is usually sufficient in the collimator.

In the prism instrument, a straight slit gives a parabolic image. By using a curved slit, one region of spectrum may be observed with straight lines; but in observing for wave lengths it will always be necessary to measure the curvature of the line or to eliminate this effect by interchanging the position of the unknown spectrum for half the observations. If both spectra have pursued identical paths in the instrument, this latter precaution is obviously unnecessary.

The prism is usually used for interpolating, in which case any convenient form of dispersion curve may be used. For extrapolating, the Hartmann formula should be employed, the constants being derived from four or more known lines. The exponent of $(n-n_0)$ may often

be omitted if the formula is used for interpolating. Denote the unknown wave length by λ and the micrometer setting on the line by n, then the formula becomes

$$\lambda = \lambda_0 + \frac{C}{(n - n_0)}$$

in which for our purposes C, n_0 and λ_0 may be considered to be empirical numbers.

One should become familiar with the various types of spectroscope and choose that most convenient for his problem. The constant deviation prism is a very handy auxiliary, as it allows the region of spectrum to be changed without disturbing any of the apparatus other than to rotate the prism. The Littrow type of mounting has the advantages of cheapness of construction and compactness, permitting easy control of temperature and vibration. In this style of mounting, a single quartz prism corrects itself for rotatory dispersion, which in other forms of mounting must be eliminated in other manners. The mirror is sometimes silvered on the last prism face. By interchanging a plane grating for the prism and mirror, the instrument may be converted into a grating spectrograph. Fabry and Jobin[19] describe a useful convertible type of spectrograph. The Littrow mounting has the disadvantages of several reflections that must be overcome, and of working off the axis of the lens: This latter is no great disadvantage if the lens is designed to have a large field.

GRATINGS.—The plane grating may be mounted with a single lens in the Littrow form, or with both collimator and camera lenses. The use of lenses assures achromatism of the overlapping orders at only a few points in the spectrum. Thus the first order at 8200A may be in exact focus with the second at 4100A (or second at 8200A and fourth at 4100-A); and the third at 6000A may be in focus with the fourth at 4500A; the second at 9500A with the fifth at 3800A: the writer has used these overlapping orders in perfect focus in various plane grating spectrographs. Complete achromatism is obtained by the use of mirrors for collimator and camera. A spectrograph using a plane grating and one mirror is useful for some purposes. In this and other forms of mounting, the tilt of the mirror and consequent astigmatism may be reduced by turning the beam from the slit through an angle of 90° by means of a prism or mirror set near the ends of the grating rulings, or set in front of the center of the grating, if the light so lost may be spared.

The concave grating may be mounted in a style similar to that of the Littrow mounting of the plane grating, the Eagle[20] design. In this form the astigmatism is somewhat greater and the lines are somewhat more curved than in the other types of mounting to be mentioned. But the compactness of the Eagle mounting, and the consequent ease with which it may be made rigid and insulated from temperature changes, and the simplicity of adjustment, recommend this form of mounting highly.

The classical Rowland mounting is familiar to all. A lack of rigidity and some difficulty in controlling the temperature have been encountered in the use of the mounting. These troubles may be eliminated in various ways: Attention is called to the Mt. Wilson vertical mounting[21] as one of the best means to this end. The Abney type is similar to the Rowland, differing in that the slit is movable while the grating and camera remain rigidly fixed to piers. Both of these types give the so called normal spectrum, an advantage growing less with increasing number of standard wave lengths.

Paschen has mounted a grating so that all parts remain fixed. If the slit and grating are separated by an amount equal to, or less than, the radius of curvature of the latter, the various orders are in focus on a circle whose diameter is this radius of curvature, and which passes through the slit and grating. It is only necessary to build the camera along this circle in order to permit the photography of any wave length in any order. This form of mounting, by permitting the photography of the whole spectrum at once, might make the best use of a small sample of a rare material. However, the mounting in parallel light gives a spectrum of such great intensity, particularly in the red and infrared, that the total time of exposure will be less in covering the whole spectrum, even though only 800A may be observed at a time by the last mentioned means.

The parallel light mounting[7D] shows but little astigmatism, and this may be eliminated entirely on the normal to the grating. This is the only mounting of the concave grating that can be used in interference work. Since the image is nearly stigmatic, this design may be used to compare the spectra of sources whose images fall on different parts of the slit. The instrument is compact, easy to adjust and to make rigid, and fairly free from temperature changes. The last mentioned advantage is due in part to the short exposure time required with this style of mounting. The image has been rated as four times more intense than that of the Rowland mounting, but this ratio depends on

the astigmatism present in the other types of mounting, and this in turn is proportional to the wave length, becoming very great in the red and infrared. The same grating, mounted in parallel light, will photograph 9000A in one-tenth the time required in the other forms of mounting.

GHOSTS.—All gratings examined by the writer show a type of ghost discovered by Lyman.[22] Since these are very faint in comparison with the intensity of the principal line, they are seldom troublesome in the region of spectrum to which the photographic plate is most sensitive. In the infrared and in the extreme ultraviolet these spurious lines may photograph more readily than the true spectrum. They are avoided in the infrared by the use of screens which are opaque to the shorter waves. In the ultraviolet their exclusion is practically impossible and they must be found and eliminated by measurement. The type of ghost shown by a particular grating may be found by observing visually the position of false lines due to the yellow line of helium. A photograph of the *He* spectrum, taken through a yellow screen and using a plate sensitive to yellow, furnishes a sure and convenient means of locating these ghosts. They are always located near to fractions of the principal line, the numerators being successive numbers, and the denominators being small numbers, (3 and 5 found to date) one denominator being characteristic of any particular grating.

PHOTOGRAPHIC PLATES.—For the region shorter than 1850A, Schumann plates must be used. These can now be purchased, yet many observers prefer to make their own, essentially by the method of Schumann.[23] Satisfactory plates can be made by precipitating silver bromide from a weak solution containing a trace of gelatine. For 1850-3600A any fine grained "slow" plate can be used to advantage, the "fast" plates being frequently much slower in this region due to traces of coloring matter in the film. For 3600–4800A the writer prefers Seed 23, or equivalent; for the green, Seed 23 bathed in a weak solution of pinaverdol and ammonia.[24] The best dye for the yellow, and red to 6750A is pinacyanol; kryptocyanin is excellent for 7000–7700A and dicyanin sensitizes for the red and infrared to 9900A, but at no point gives a sensitivity equal to the maximum of pinacyanol in the red. The fast emulsions can be substituted for Seed 23 with profit whenever a weak image of a faint line will suffice. If full exposure is to be given, the fast plate is not greatly superior in speed, and has the decided disadvantage of bad grain. Certain commercial plates are sensitive to the green; panchromatic plates are sensitive as far as the deep red. The speed of

commercial color sensitive plates can often be greatly increased by bathing in a weak aqueous solution of ammonia.[24]

The writer has found no great advantage in using any particular kind of developer. For spectra the observer may well use any non-staining developer with whose performance he is familiar.

COMPUTING HINTS.—To a beginner, the amount of computing necessary in wave-length measurement may seem rather formidable. This view is partly due to lack of computing experience, and to failure to hit upon the most convenient method for the particular task. To some, the points about to be emphasized will seem self evident, and the subject is discussed only because the writer has encountered able physicists with years of experience still computing by methods requiring twice the necessary amount of labor. The novice can well afford to spend several days searching for means of simplifying the computing of the problem in hand, and these remarks are intended to direct his attention to methods, rather than to give the best form in any particular case.

Computations are sometimes carried out with too much rigor. If the final accuracy possible is $\pm .0005$A, there is no use in reducing the individual plates, or the means of three plates, with an accuracy greater than $\pm .0002$A. To carry reductions to one more significant figure than is warranted adds nothing but labor.

Take means at the earliest possible stage of the computing. If three plates have been taken with nearly the same adjustment of the instrument, the means of the measurements can be taken directly, or by means of very simple reduction formulas, before any other computing has been done. This procedure may save more labor in interference work than in the case of grating observations, since in the former case the formation of the reciprocals is a tedious process.

ON THE SIMPLIFICATION OF FORMULAS.—Grating, normal spectrum denote the wave length of the first standard by λ_0 and the micrometer setting on this line by n_0. The wave length, λ, of any line is found from its micrometer setting, n, by the formula $\lambda = \lambda_0 + a(n - n_0)$, "a" being the scale determined from two widely separated standards. In many laboratories it is the practice to form for each line the difference $n - n_0$, multiply it by "a," and then add λ_1 to this product: Three operations with a chance for error in each. The correct procedure for one using a computing machine of any type, is to find "a"; make this the multiplier and multiply "n_0" by it; turn the product dials to read "λ_0"; then operate by addition and subtraction until the multiplicand

dials read the successive values of "n." The product dials will then read the successive values of "λ." This procedure avoids all subtraction and adds "λ_0" automatically, saving two processes with their opportunities for error.

GRATING NEAR NORMAL.—The formula becomes $\lambda=\lambda_0+a(n-n_0)+b(n-n_0)$.[2] The remarks of the foregoing paragraph apply to the first part of this formula. To simplify the computation of the squares, the observer adjusts the plate on the comparator so that the reading on the first standard is very near to zero or to some even ten, so that the differences $n-n_0$ may be readily taken mentally. A small departure from the even ten in the case of the first standard may be neglected in computing the square term, since it will affect the reduction curve but slightly, and this curve must be plotted in any case. Again, if the coefficient "b" is nearly .0001, .005, or any number by which the observer can multiply easily, it should be made exactly this number, so that the squares can be taken from a table and multiplied mentally. The curve takes care of any slight lack of exact representation. The formula need only be consistant and convenient, and no formula should become a fetich, but remain a device designed for the convenience of the user.

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(B) Neon. Burns, Meggers, Merrill, Ibid. *14*, pp. 765–75; 1918.

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Studies on the Low-Voltage Arc in Mercury Vapor and Its Relation to Fluorescence.—This paper relates to the arc discharge between a hot filament and a cold anode through mercury vapor. In the first part Yao presents curves of "striking voltage" and "minimum maintaining voltage" versus filament-heating-current. As the filament-current is decreased from its highest value the striking voltage rises at a constant rate, from ca. 1.8 volt to about 5 volts, then increases sharply if the filament-temperature is further lowered; the maintaining-voltage is always lower than the striking-voltage. The explanation offered, in general terms, is this: (1) just before the arc strikes, there is a small electron current limited by space-charge; (2) a small portion, a, of this current consists of electrons emitted with energies high enough to ionize the mercury atoms (by double impact) when added to the energy imparted by the accelerating field; (3) when the arc strikes the space-charge is neutralized, and the electron-current is increased, often more than a hundredfold; (the number of high-energy electrons is proportionately increased, and now (4) the accelerating voltage may be cut down until the number of electrons fast enough to ionize is reduced to the original value a, without extinguishing the arc. This theory is formulated in quantitative terms, and an order-of-magnitude agreement is attained (using the probably erroneous assumption that the mean energy of the electrons just emitted is $3\,kT$ instead of $3kT/2$). In the second part data are given which show that the striking-voltage is somewhat less when the liquid mercury surface with which the mercury vapor is in equilibrium is close to the path of the discharge, than when it is 50 cm or more distant. The values found for the difference fluctuate considerably, but the mean value agrees with the theory that the valence-electron of the mercury atom can be lifted from its stable ($1S$) orbit into the ($2p_2$) orbit, receiving 4.9 volts of energy, only when the atom is freshly evaporated from the liquid; otherwise it can be lifted only into the ($2P$) orbit, requiring 6.7 volts. This is in consonance with observations on the excitation of the corresponding line (2536) in fluorescence. [Y. T. Yao, (Princeton) Phys. Rev., *23*, pp. 1-21; 1923.] KARL K. DARROW

The Continuous X-Ray Spectrum; Intensity as a Function of Wave Length and Atomic Number. –Using a gas-discharge X-ray tube; a voltage of 10 470; targets of Al, Cu, Ag, Sn, and Pt; a rocksalt crystal to resolve the radiation, and an ionization-chamber to measure it, Wagner and Kulenkampff have determined the intensity versus wave length relation for the radiation in the range from 2.6 A to the upper frequency limit at 1.2 A. A formidable array of corrections is required; first there is a separate determination of the reflecting power of the crystal as a function of wave length; then the correction for absorption of X-rays by the depth of the target which they traverse while escaping, apparently performed by measuring the radiation emitted at right angles to the incident electron stream for various angles of incidence of this latter, and then extrapolating to the case of grazing incidence and normal emergence; finally, corrections for absorption in the Al window of the tube and for incompleteness of absorption in the ionization-chamber. When all these corrections are made the data are altered by as much as "several hundred per cent" in some cases, and the curves have an entirely different form. The intensity versus frequency curve for each metal now starts from the frequency axis at the quantum-limit eV/h, and, as we go towards lower frequencies, bends over into a straight upward slanting line, which continues straight as far as the observations extend. The slope of this line is proportional to Z, the atomic number of the metal; so is the distance from the point where (prolonged) it intercepts the frequency axis, to the actual intercept at eV/h. Observations on silver indicate that when the primary voltage is changed the whole curve is merely shifted sidewise, remaining parallel to itself. [E. Wagner and H. Kulenkampff (Munich). Phys. ZS. *23*, pp. 503–506; 1922; also Annalen *68* and *69*]. KARL K. DARROW

Spectroscopic Measurement of the Electron Affinity of Chlorine.—Pure chlorine was streamed through a Geissler tube of the capillary type. The discharge excited by a small induction coil was viewed end-on with a quartz spectrograph. This was found to be a favorable condition for exciting the continuous spectrum. It extends from $\lambda = 3180$ to the ultraviolet limit of the spectrograph with marked maxima at $\lambda = 3070$ and $\lambda = 2570$. This continuous band ends rather abruptly on the red side at $\lambda = 3180 \pm 10$. It apparently corresponds to the iodine and bromine bands ending at $\lambda = 4800$ and $\lambda = 4200$ respectively. Franck has proposed the theory that these continuous spectra result when an electron is drawn into the atom by the electron affinity, the energy lost by the electron being radiated. It follows that the quantum determined by the red limit of the band will be proportional to the electron affinity, E. For chlorine $\lambda = 3180$ gives $E = 89.3$ calories per mol. The value determined by Born from thermodynamical data is $E = 119$ calories/mol. While the agreement is not very good it may be significant that the ratio of E determined by Born to E determined spectroscopically is in all three cases about 1.3. This work is part of a more extensive study of the chlorine spectrum which will be published later. [E. v Angerer., ZS. f. Phys. *11*, p. 157; 1922.]

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INSTRUMENT SECTION

METHODS AND APPARATUS IN SPECTRORADIOMETRY

By W. W. Coblentz

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The difficulties experienced by earlier workers in spectroradiometry are gradually being overcome by the development and application of apparatus suited for the purpose. It is essential to use spectrometers of high light-gathering power.

The essential parts of a spectroradiometer consist of (1) a suitable spectrometer for dispersing thermal radiation into a spectrum, and (2) suitable radiometric instruments for measuring the spectral radiation intensities.

1. The Spectroradiometer

Ultraviolet Spectrum.—For measuring thermal radiation intensities in the ultraviolet part of the spectrum one may use a spectrometer having achromatic lenses of quartz-fluorite. However, the scarcity of clear fluorite for large-sized lenses makes such apparatus very expensive.

Pflüger (Ann. der Phys. (4), *13*, p. 890; 1904) used simple lenses of fluorite 4 cm in diameter (32 cm focal length) and a fluorite prism. An inexpensive spectroradiometer of high light-gathering power was made by Coblentz (B. S. Bulletin *7*, p. 245; 1911) by using simple plano-convex lenses (6 cm in diameter and 20 cm focal length) and a prism of quartz. Pfund (Phys. Rev. (2) *7*, p. 289; 1916) has described similar apparatus in which the radiometer is kept in focus automatically in different parts of the spectrum.

The apparatus may be designed also as an illuminator for separating the visible from the ultraviolet of, for example, the sun or of a quartz-mercury vapor lamp. (Coblentz and Kahler, B. S. Sci. Papers, No. 16, p. 233; 1920.)

Visible Spectrum.—For spectroradiometric measurements in the visible spectrum and the infrared to about 0.8μ ($\mu = 0.001$ mm) one can use a spectrometer with visually achromatized lenses of glass. Here, also, it is desirable to use apparatus having a high light-gathering power, such as one obtains with lenses 6 cm in diameter and 20 cm focal length. (Coblentz, B. S. Bulletin 10, p. 36 (Fig. 5); 1913.)

Infrared Spectrum.—Owing to the opacity of prism and lens material for infrared rays, also owing to the fact that a concave mirror is achromatic, reflecting mirrors have been used almost exclusively for infrared spectral radiation intensity measurements. In the infrared spectrum beyond 2μ most of the metals have a very high reflecting power (90 to 98 per cent), and concave metal mirrors or metal-on-glass mirrors are, therefore, especially useful for infrared investigations.

Recent designs of spectrometers having collimating and image-forming mirrors are described in papers by Coblentz (B. S. Bulletin, *10*, p. 1; 1913) and by Gorton (Phys. Rev. (2), *7*, p. 66; 1916). Vacuum spectrometers have been described and used by Trowbridge (Phil. Mag. (6), 20, p. 768; 1910) and by McCauley (Astrophys. Jour., *37*, p. 164; 1913).

For determining the energy distribution in the spectrum of the sun's rays Langley (Annals Astrophys. Obs., 1; 1905) used an image forming mirror of great focal length. For average laboratory work using terrestrial sources which are weak in radiation, the average focal length of the mirrors is 40 to 50 cm. Such mirrors should be 10 cm in diameter, (and the prism faces should be correspondingly large) in order to obtain a high light-gathering power.

The optical parts of a simple mirror spectroradiometer are illustrated in Fig. 1 in which S_1 is the entrance slit, C is the collimating

mirror, P is the prism, I is the image forming mirror, S_2 is the exit slit, and T is the radiometer. It is usually necessary to keep the spectroscope arms fixed. In this case the spectrum is moved over the radiometer (exit slit S_2) by mounting an extra mirror M upon the prism table, with its axis of rotation passing through the axis A, of the spectrometer. This is the Wadsworth mirror-prism system. (Phil. Mag. (5) *38*, p. 346; 1894.) The source of radiation R may be focused upon the spectrometer slit by means of a mirror.

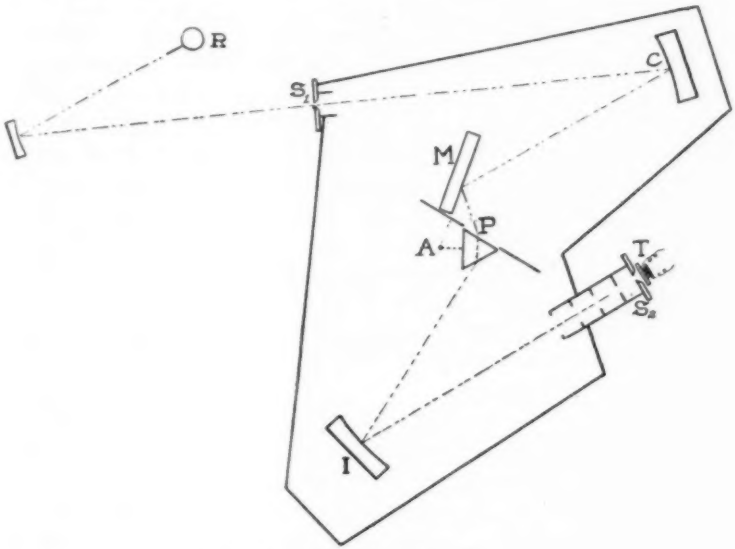

FIG. 1. *Mirror spectroradiometer.*

The mirrors being astigmatic, the exit slit is placed at the vertical focus of the spectrum (spectral line).

A quartz prism is useful to measure radiation to 3μ; a fluorite prism to 10μ; rock salt to 15μ; and sylvite to 20μ.

To obtain measurements on homogeneous radiation of wave-lengths greater than about 20μ it is necessary to resort to special expedients. Now that the bands of high selective reflection are known one can isolate fairly homogeneous radiations by multiple reflection from surfaces of various substances, e.g., quartz, fluorite, rock salt, etc. However, in studying new substances for residual rays it is customary to proceed as described in the two following captions.

Wire Gratings: Residual Rays.—Beyond 20μ all substances, thus far observed, are too opaque to be useful for prisms. Instead of a prism, a diffraction grating of fine wire (0.2 to 0.3 mm) is used. (Rubens and Nichols, Ann. der Physik, (3) *60*, p. 418; 1897; and Coblentz, Publ. No. 97, p. 25, Carnegie Inst. Wash., 1906.) Residual rays, which are obtained by multiple reflection from several surfaces of a substance, say rock salt, enter the spectrometer slit and are analyzed by the grating. By this means bands of selectively reflected heat waves from 50 to 100μ have been isolated.

Extra-focal Isolation of Homogeneous Rays.—The loss of energy in the wire grating method of isolating long heat rays is very great. The longest heat rays (300μ) yet isolated have been obtained by taking advantage of the fact that quartz is transparent to thermal radiation of wave-length greater than 50μ, and of the fact that a simple convex lens is not achromatic. By means of suitable diaphragms over the quartz lens the ultraviolet rays have been separated from the visible rays (Lenard, Ann. der Physik, (4), 1, p. 486; 1900). In the same manner the long infrared rays have been isolated (Rubens and Wood, Sitzber, Akad. Wissensch. Berlin, 52, p. 1122; 1910) and studied. The apparatus required is simply a large quartz lens for isolating the rays (obtained from a quartz-glass, mercury vapor lamp) and a radiometer for measuring the intensity.

A brief summary of investigations in the long wave-length infrared spectrum will be given by Weniger in an early issue of this Journal.

Spectrometer Calibration.—In most spectroradiometric work it is necessary to know the wave-lengths at which the thermal radiation intensities are measured. In the visible spectrum it is an easy matter to note the spectrometer settings for the emission lines of some source (for example, the mercury arc, or helium gas in a Plücker tube) the wave-lengths of whose emission lines are known. Similarly, in the ultraviolet, the emission lines of mercury, cadmium, zinc, etc., may be noted with a fluorescent canary glass, a fluorescent screen, or radiometrically with a thermopile (Pflüger, Ann. der Phys. (4), 13, p. 890; 1904) or bolometer.

The spectrometer circle may be calibrated for wave-lengths in the infrared spectrum to 1μ, by noting the emission lines (Paschen, Ann. der Phys. (4), 27, p. 537, 1908; 29, p. 625, and 30, p. 746, 1909; 33, p. 717, 1910) of sodium and potassium in a carbon arc; also the emission lines of a quartz mercury vapor lamp and helium in a vacuum tube, and the

emission bands of oxides (Coblentz, B. S. Bulletin, 2, p. 457, 1907; 7, p. 661, 1911).

Beyond 2μ, where the emission lines are usually weak (except the strong emission band of carbon dioxide at 4.4μ in the bunsen flame), one can calibrate the prism by noting sharp absorption bands (Coblentz, B. S. Bulletin 7, p. 652, 1911; also Publ. Nos. 35, 65 and 97, Carnegie Inst., Washington) such as, for example, the bands of sylvite, *KCl*, at 3.18μ and 7.08μ respectively.

For work requiring great accuracy, the proper method of calibration is by calculating the minimum deviation settings for different wave-lengths, using the refractive indices and the angle of the prism. For this purpose, the yellow sodium lines, or, better, the yellow helium line, $\lambda = 0.58758\mu$, is used as a reference point on the spectrometer circle. The minimum deviation settings for the various infrared wave-lengths are computed from the corresponding refractive indices, and referred to the yellow helium line as a basis. After this, the bolometer or thermopile is adjusted upon the yellow helium line, then on rotating the spectrometer through a certain angle, say 2°, the corresponding wave-length is, say 6μ, while a rotation of 4° places the bolometer at about 8.7μ in the spectrum of a 60° fluorite prism (Coblentz, B. S. Bulletin, *10*, p. 49; 1913).

Reduction of Data from Prismatic to Normal Spectrum.—In order to reduce an observed spectral energy distribution of an incandescent substance from a prismatic to the normal spectral intensity it is necessary to correct the observations for absorption of radiation by the mirrors and by the prism. The proper formula for eliminating the absorption in a wedge is given by Paschen (Sitzber, Akad. Wiss., Berlin, *22*, p. 405; 1899), and by Coblentz (B. S. Bulletin, *11*, p. 471; 1914), who gives also the numerical factors for eliminating the absorption in a wedge of quartz. Factors must be applied also for reducing the data from the prismatic to the normal spectrum. Recent examples of this type, in cases where the refractive indices are known, are given in papers by Coblentz (B. S. Bulletin *10*, p. 1; 1914) and in cases where the refractive indices are not known (B. S. Bulletin, *13*, p. 355; 1916).

Elimination of Scattered Radiation in Spectral Energy Measurements.—In a mirror spectrometer it is desirable to have the optical parts enclosed to exclude stray light; also to keep out dust and to preserve the silvered mirrors (Coblentz, B. S. Bulletin, *7*, p. 221; 1910). The image-forming telescope tube should be large and suitably diaphragmmed

so that, when the violet end of the spectrum is incident upon the radiometer receiver, the infrared end of the spectrum cannot be reflected from the side of the tube and impinge upon the receiver. Furthermore, the beveled edges of the slits of the spectrometer should face outward (Coblentz, Jour. Franklin Inst., *175*, p. 151; 1913; B. S. Bulletin, *14*, pp. 229 and 534; 1918) instead of facing the image-forming mirror lens, as usually obtains in commercial instruments.

By using suitably constructed optical instruments, the scattered radiation is practically eliminated. What little remains may be obviated by using, before the entrance slit of the spectrometer, a shutter [Rubens (with Nichols and with Trowbridge), Ann. der Phys. (3), *60*, pp. 418 and 724; *61*, p. 225, 1897; Pfund, Phys. Rev., (2), *7*, p. 289; 1916.] which is opaque to the region of the spectrum under investigation but which transmits the scattered radiations. In this manner the scattered radiations are incident upon the radiometer all the time and, hence, do not affect the energy measurements. Using a spectrometer which is provided with slits and diaphragms, as just mentioned, the (Coblentz and Kahler, B. S. Sci. Papers, No. 16, p. 233; 1920) scattered radiations are immeasurable, and hence negligible, in comparison with the intensities under investigation.

2. RADIOMETRIC INSTRUMENTS

Under this caption a brief outline is given of the most important radiometric instruments for present day laboratory work in thermal radiation. A summary of the instruments and methods used in the measurement of solar, sky, nocturnal and stellar radiation, is given in a paper by Coblentz (Jour. Op. Soc. Am., *5*, May, 1921). The study of polarization phenomena by means of spectroradiometry requires special apparatus which is summarized in a paper by Ingersoll (Jour. Op. Soc. Am., *5*, p. 156; 1921).

Radiometric instruments are used for two classes of work: (1) the measurement of total radiation, and (2) the measurement of thermal radiation intensities in the spectrum. The latter differs from the former only in that the radiometer receiver for absorbing thermal radiation has to be long and narrow in order to correspond with the spectrometer slit. Various details on the construction and operation of bolometers, thermopiles, etc., are given in papers by Coblentz (B. S. Bulletin, *4*, p. 391, 1907; *9*, p. 7, 1912; *11*, p. 131, 1914; *13*, p. 423, 1916; *14*, p. 507, 1918), on "Instruments and Methods of Radiometry." A concise exposition of the whole subject of radiometry and spectroradiometry is given

in Nutting's "Outlines of Applied Optics." The instruments and methods and reduction formulas used in the various determinations of the constant of total radiation and of spectral radiation are summarized in recent papers by Coblenz (B. S. Sci. Papers, No. 17, p. 8, 1920, and Jour. Op. Soc. Am., *5*, p. 131, Mar., 1921).

One of the chief complaints of workers in radiometry is the uncertainty of the observations caused by unsteadiness of atmospheric conditions. Radiometers are essentially of small heat capacity and as a consequence are greatly affected by air currents. In planning a research, it is therefore desirable to place the radiometer in a container that can be evacuated, or to make the observations on dull, cloudy, windstill days, or in the summer when the air is more uniformly heated within and without the laboratory.

The loss of heat by convection is very great. The sensitivity of a modern thermopile is doubled and that of a thermocouple of fine (0.01 mm) wire is quadrupled, by placing it in an evacuated enclosure.

Most of the radiometers to be discussed are nonselective in their response to thermal radiation of all wave-lengths, and this sometimes causes difficulties. Hence in investigations employing ultraviolet radiations, (for example, ultraviolet transmission and reflection measurements) it is sometimes advisable to use a selective radiometer such as, for example, a potassium hydride photo-electric cell which is sensitive only to the visible and the ultraviolet.

Thermopiles.—Thermopiles are constructed of fine wires of different kinds of metal as for example copper and constantan. They function by generating an electric current when the alternate junctures of these two metals are heated by absorption of thermal radiation. The thermopile is therefore less effected by air currents than a bolometer which is slightly warmer than the air as a result of the electric current constantly flowing through the circuit. Improvements introduced during the past few years have made the thermopile a close competitor with the bolometer in sensitivity. It is not so quick in response as is a bolometer, requiring three to five seconds to attain a maximum. However, there are but few everyday problems requiring instantaneous action.

The temperature rise being small, the thermoelectric current generated is proportional to the heat absorbed and hence proportional to the intensity of the incident radiation.

The theory of thermopile design has been worked out by Altenkirch (Phys. Zs., *10*, p. 560; 1909) and by Johansen (Ann. d. Phys., (4), *33*,

p. 517; 1910). The latter finds that (1) the resistance of the thermopile should equal that of the galvanometer, (2) the radii of the two wires of the element should be so chosen that the ratio between the heat conductivity and the electrical resistance is the same in both, (3) the heat loss by conduction through the wires should equal the heat loss by radiation from the junctions, (4) the radiation sensitivity is proportional to the square root of the exposed surface. In an iron-constantan couple the theory required the use of iron wire 0.023 mm and constantan wire 0.045 mm diameter; and for a Bi-Fe couple iron wire 0.024 mm and bismuth wire 0.075 mm diameter. If the diameter of both wires were twice as great, theory indicates that the sensitivity would be only 0.8 the maximum sensitivity.

The technique of rapid construction of thermopiles of bismuth and silver is given in papers by Coblentz (B. S. Bulletin *4*, p. 400, 1908; *9*, p. 15, 1912). In a separate paper (B. S. Bulletin, *11*, p. 141; 1914) various modifications of thermopiles having a continuous absorbing surface are described, suitable for physical photometers, for physiological investigations, for the measurement of nocturnal radiation, etc. The construction of thermocouples for measuring heat from stars (Coblentz, B. S. *11*, p. 613; 1915) requires considerable skill and special technique. For ordinary laboratory work Bi wire (0.1 mm) with receivers of tin (2 by 1 by 0.02 mm) are used. After completion the silver wire is given a thin coating of shellac. Such thermopiles are strong and can be shipped without breakage.

Symmetry of construction is important in a thermopile. To attain this end all the junctures should be suspended freely in the air which becomes warmed by the incident radiation. Thermopiles in which the "cold" (unexposed) junctions are soldered to metal supports invariably cause a drifting of the galvanometer as a result of warming of the air surrounding the "hot" junction. This can be neutralized by having a thermocouple of low emf (e.g. iron-copper) in the circuit. By slightly heating one of the junctures of this couple, the zero position of the galvanometer reading is brought back on the scale.

The radiation sensitivity of a thermopile is doubled by placing it in a vessel evacuated to 0.02 mm pressure. The radiation sensitivity of thermopiles of fine (0.02 mm diam.) wire is increased four to five times in a vacuum.

For additional information on iron-constantan thermopiles the reader is referred to papers by Rubens (Zs. Instrk., *18*, p. 65; 1898), by Paschen (Ann. der. Phys., *33*, p. 736; 1910, and by Reinkober (Ann. der Phys.,

(4), *34*, p. 349; 1911; Phys. Zs., *14*, p. 998; 1913). The latter gives a valuable intercomparison of vacuum thermopiles.

Bolometers.—The electrical connections of a bolometer (Langley, Proc. Amer. Acad. Sci., *16*, p. 342; 1881) and its auxiliary galvanometer are the same as that of a Wheatstone bridge. The latter is constructed of resistances having a negligible temperature coefficient. It is therefore misleading to speak of the bolometer as being "simply a Wheatstone bridge." In a bolometer two branches of the bridge are made of thin strips of metal having a high temperature coefficient of resistance. These strips, called receivers, are made as thin as possible in order to reduce the heat capacity. They are usually made of thin (0.001 mm) platinum, though iron and nickel have also been used. They are blackened to increase the absorption of radiation. Two strips are used for symmetry. The remaining two branches of the bridge are usually made of manganin wire having three to four times the resistance (Abbot, Astrophys. J., *18*, p. 1; 1903) of the receivers.

It will be understood that the bolometer functions as a result of a change in resistance of one of these thin blackened strips when it is exposed to radiation. The resulting galvanometer deflection is proportional to the temperature rise (change in resistance) of the exposed receiver and hence of the intensity of the thermal radiation stimulus.

Convection currents of air cause great unsteadiness in a bolometer. It is therefore necessary, in practically all work, to place the receivers in a vessel from which the air can be evacuated to a pressure of less than 0.01 mm (Coblentz, B. S. Bulletin, *4*, p. 415, 1908; *9*, p. 34, 1912.) The vacuum bolometer (Warburg, Leithauser and Johansen, Ann. der Phys., (4), *24*, p. 25, 1907; Liembach, Ann. der Phys., (4), *33*, p. 308, 1910; Buchwald, Ann. der Phys., (4), *35*, p. 928, 1910) is much more sensitive than a bolometer in air. However, there are many complications and disturbances, and recent improvements in the sensitivity of thermopiles have made it possible to substitute the latter in most radiometric work.

Important applications of the bolometer in studying polarization phenomena, especially in the infrared are given in a paper by Ingersoll (Phil. Mag. (6), *11*, p. 41; 1906).

Radiomicrometers.—The radiomicrometer is essentially a moving coil galvanometer having a single loop of wire with a thermojunction at the end. This instrument was invented independently by d'Arsonval (Soc. Franc. de Phys., pp. 30 and 77; 1886) and by Boys (Proc. Roy. Soc., 42, p. 189, 1887; Phil. Mag. *180A*, p. 159; 1889). Coblentz (B. S.

Bulletin, *2*, p. 479, 1906; *7*, p. 243, 1911) has devised a vacuum radiometer which combined the principle of the radiomicrometer and the Nichols radiometer. One of the most noteworthy radiomicrometers was constructed by Schmidt (Ann. der Phys., (4), *29*, p. 1003; 1909) in the laboratory of the late Prof. Rubens. The instrument has undergone modifications by the latter (Rubens and Hollnagel, Sitzber Akad. Wiss., *4*, p. 26; 1910) and, judging from published work, is practically the only one now in use. The commendable feature of the radiomicrometer is its freedom from magnetic disturbance. However, it is not portable, and to attain a high sensitivity requires a long period.

Nichols Radiometer.—The torsion radiometer of Crookes as improved by Nichols (Phys. Rev., *4*, p. 297; 1897) consists essentially of two similar, thin vanes of blackened mica or platinum, attached to a horizontal arm and suspended, by means of a fine quartz fiber, in a vessel which is evacuated. The vanes are about 3 mm from a window. The radiation to be measured falls upon one of the vanes which becomes warmed and repelled from the window. A small mirror is attached to a glass staff which supports the vanes. The deflection is measured by means of a telescope and scale. The device is free from magnetic disturbances but to attain high sensitivity it requires a long period, say 30 to 60 seconds, as compared with a thermopile and Thomson galvanometer which requires 5 seconds. In its time it was very useful, but at present it is being replaced by vacuum thermopiles and iron-clad Thomson galvanometers. Further details concerning this radiometer may be found in the following papers: Stewart, Phys. Rev., *13*, p. 257, 1901; Drew, Phys. Rev., *17*, p. 321, 1903; Porter, Astrophys. J., 22, p. 229, 1905; Coblentz, Pub. No. 35, Carnegie Inst. of Wash., 1905; and B. S. Bulletin *4*, p. 404, 1908.

Galvanometers.—One of the most important adjuncts to a radiometric laboratory is a magnetically well-shielded astatic galvanometer. The bolometer and the thermopile require an auxiliary galvanometer. Much radiometric work can be done with a thermopile and a sensitive d'Arsonval galvanometer. Such galvanometers, now constructed by Leeds and Northrup and by Weston, have a sensitivity of 1×10^{-9} ampere. They are designed to fit a bismuth-silver thermopile having a resistance of 10 to 12 ohms. In other words they are designed to be critically damped on an external resistance of 12 ohms and a single swing of 8 to 10 seconds. Similar moving coil galvanometers having a resistance of 20 000 to 40 000 ohms are useful in radiometry in which use is made of a photoelectric cell for the radiometer.

Recent great advances in radiometry have resulted from imbedding the coils of a Thomson galvanometer in soft iron (Coblentz, B. S. Bulletin, *4*, p. 431, 1908; *9*, p. 60, 1911) and providing laminated shields of transformer iron. Tests by Coblentz (B. S. Bulletin, *13*, p. 423; 1916) showed that while the inner shields of laminated iron greatly reduced the magnetic disturbances, imbedding the coils in blocks of soft iron, reduced still further the effects of air currents and magnetic perturbations.

The galvanometer should be permanently mounted upon a substantial pier. Local tremors are sometimes avoided by shifting the position of the galvanometer. Serious earth tremors may be avoided by suspending the galvanometer as described by Julius (Ann. der Phys., (3), *56*, p. 151; 1895).

A good shield from the magnetic disturbances of the average laboratory is obtained by imbedding the coils in blocks of soft (Norway) iron, over which is placed a laminated shield of soft iron. The latter is made of 20 or more strips of transformer iron about 75 cm (2.5 ft.) in length and 16 cm wide and weighing 9 to 19 pounds. It is well to provide additional shields of black wrought iron welded pipe of "extra strong" quality in sizes 5, 7, 9, and 11, (See Kent's Mech. Eng. Pocketbook) and cut in lengths of 25 or to 30 cm. Researches not requiring the highest radiometric sensitivity have been made successfully by the writer by using simply the iron-clad mounting and laminated cylinder just described, and one additional shield which consisted of an 8-inch black, wrought-iron pipe, inside of which was placed a series of laminations of transformer iron, which practically doubled the thickness. A cover of pieces of transformer iron adds to the shielding effects and keeps out dust.

Further information concerning iron-clad galvanometers is to be found in the following papers:

Dubois and Rubens, Ann. der Phys., (4), *2*, p. 84, 1900;
Mendenhall and Waidner, Amer. Jour. Sci., *27*, p. 249, 1907;
Abbot, Astrophys. Jour., *18*, p. 1, 1903;
Wills, Phys. Rev., *24*, p. 243, 1907;
Nichols and Williams, Phys. Rev., *27*, p. 250, 1908;
Paschen, Phys., Zs., *14*, p. 521, 1913.

Vacuum Maintenance.—The most efficient device for maintaining a vacuum is metallic calcium (Coblentz, B. S. Bulletin, *11*, pp. 141 and 613, 1914; Jour. Op. Soc. Am., July, 1921) in a quartz or porcelain tube which is cemented to the thermopile container. Heavy pyrex tubing is

useful but is likely to collapse on heating. At the beginning the thermopile container is thoroughly evacuated by means of an oil pump and the stop-cock is closed.

The metallic calcium should be free from carbide, and should be heated to a dull red before closing the stop-cock. After this the vacuum is maintained by heating the calcium to a dull red by means of an alcohol lamp, a gas flame, or by electric means. The vacuum stellar thermocouples were heated but twice in six years, to remove the gases liberated from the cell walls. On the other hand a laboratory thermopile which has always leaked badly has its vacuum maintained by frequently heating the calcium.

3. LIGHT SOURCES

Under this caption light sources are described which are suitable for spectrophotometric and spectroradiometric work.

Fundamental Candlepower Standards.—Among the primary standards of luminous intensity are the *Sperm Candle* and the *Hefner-Alteneck* amyl acetate lamp. They are subject to great fluctuations in intensity, owing to humidity, air currents, etc., and hence are maintained primarily for use in the national laboratories, for example, in the National Bureau of Standards.

The unit of luminous intensity is best maintained, as a working standard "*secondary standard*" in the form of seasoned incandescent lamps. This secondary standard was obtained by an elaborate intercomparison of seasoned incandescent lamps which were interchanged among the foreign national laboratories. It is easily operated and not subject to fluctuations such as obtain in the standard candle. Copies are easily obtainable. Hence experimenters interested in obtaining luminous intensity measurements, of high accuracy, should provide themselves with seasoned incandescent lamps, the candlepower of which has been certified by a national laboratory, or any laboratory where accurate copies of the primary standard are maintained.

Radiation Standards are useful in many problems in botany, physiology, psychology, etc., in which light stimuli are used. These light stimuli should be expressed in absolute units,—gram calories or ergs. This is easily accomplished by exposing a radiometer (e.g., thermopile) to the light stimulus and then to a standard of radiation of which the energy density, per mm^2 of exposed area at a given distance

from the standard, is known. (Coblentz, B. S. Bulletin *11*, p. 171; 1914.)

For very accurate work the National Bureau of Standards has compared seasoned incandescent lamps with a uniformly heated radiator or so-called black body, which is the primary standard of radiation in absolute value. For less refined work it is sufficient to use the total radiation from a standard sperm candle, or Hefner lamp, of which the energy density, in absolute units, has been determined by Coblentz (B. S. Bulletin *11*, p. 87; 1914). Assuming that the coefficient of total radiation of a black body is 1.36×10^{-12} gr. cal. cm^{-2}. $deg.^{-4}$ $sec.^{-1}$, the total radiation per cm^2 per sec. at 1 meter from a standard sperm candle is 29 microcalories and that of a Hefner lamp (without a diaphragm) is 26 microcalories.

Ultraviolet Spectrum.—The mercury vapor lamp has undergone great improvements during the past few years. The emission spectrum of incandescent mercury vapor in a quartz lamp is a powerful source of emission lines, from 0.25μ to 1μ. Radiometric measurements are illustrated in papers by Souder (Phys. Rev., *8*, p. 316; 1916) and by Coblentz, Emerson, and Long (B. S. Bulletin, *15*, p. 1; 1918).

The emission lines at 0.305μ, 0.313μ, 0.365μ, 0.406μ, 0.436μ, 0.546μ, and 0.579μ are of great intensity and, since they are few in number, one can use a wide slit thus gaining in intensity. Equipped with a Cooper-Hewitt, 110-volt, 400-watt quartz mercury vapor lamp the experimenter is now able to make thermoradiometric measurements, at certain wavelengths in the ultraviolet, with as great ease and accuracy as in the infrared. Owing to the generation of ozone this lamp should be operated in a closed metal box provided with a ventilator. Deep-brown colored glasses should be worn when exposed to the lamp, otherwise painful and perhaps permanent injurious effects will occur to the eyes. The painful effects are not felt till about 5 hours after exposure.

Between 0.2μ and 0.3μ the emission lines of mercury are rather weak, radiometrically. But they are easily observed by allowing them to impinge upon white (blotting) paper covered with anthracene or some other fluorescent substance. To impregnate the screen with the fluorescent material, the anthracene is dissolved in benzol which is then poured over the paper.

For making radiometric transmission and reflection measurements in the ultraviolet between 0.18μ and 0.28μ using a vacuum thermopile, one can employ the strong lines from the spark (using a condenser) spectra of *Al*, *Cd*, *Mg*, and *Zn*. (Pflüger, Ann. der Phys., (4) *13*, p. 890,

1904; Coblentz, Jahrb. Radiovaktivität und Elektronik, *8*, p. 177, 1910). Quartz and fluorite apparatus must be used since glass is opaque to radiations of wave-lengths less than 0.28μ. These spark lines are very intense and they are likely to injure the eyes unless glasses are worn.

A source of ultraviolet radiation, which gives practically a continuous spectrum, has been described by Howe (Phys. Rev., (2) *8*, p. 674; 1916; and Tyndall, B. S. Tech. Paper No. 148, p. 26, 1920.). It consists essentially of a high frequency discharge from a Tesla coil, the electrodes being under water. This is especially useful in photographic photometry.

Descriptions of light sources for producing emission spectra in the extreme ultraviolet are to be found in papers by Lyman (Astrophys. Jour., *27*, p. 87; 1908) and by Millikan (Astrophys. Jour., *52*, p. 47; 1920).

Visible Spectrum.—Transmission and reflection measurements in the visible spectrum are now easily made, radiometrically, by using a gas-filled tungsten lamp as described by Coblentz (B. S. Bulletin *14*, p. 115; 1917). A 500-watt, "Mazda C," stereopticon type is recommended for transmission work. This type of lamp is easily calibrated for an equal energy spectrum such as was used by Coblentz and Kahler (B. S. Bulletin *15*, p. 121; 1919) in studying the photoelectric sensitivity of substances. The lamp deteriorates but slowly owing to the fact that, of the total time that it is used, only a short time is occupied in making observations at maximum (normal) voltage.

For spectrophotometric work in which it is desired to utilize a large, evenly-illuminated field of view it is customary to place a number of these lamps in a box, having a white diffusely reflecting interior. An opening in this box represents the source of radiation.

The arc between electrodes of *Al*, *Cu*, *Cd*, *Zn*, etc., also vacuum tubes of hydrogen, helium, etc., furnish strong emission lines, well spaced for calibration work in the visible and in the ultra-violet spectrum.

The iron arc is a source of hundreds of spectral lines, of accurately known wave-lengths, which are useful in comparing unknown spectral lines. Data of this type are to be found in tables of standard wave-lengths.

Infrared Spectrum.—An excellent source of radiation for transmission measurements in the infrared spectrum, to 4μ, is 250-watt or 500-watt gas-filled tungsten lamp. For reflection work it is desirable to use a

single wide strip of tungsten, such as, at this writing, is being made by the Nela Research Laboratory. An image of this incandescent strip is reflected from the sample under investigation and then focused upon the slit of the spectroradiometer.

The Nernst lamp filament is useful for obtaining a single intense, narrow source of radiation, but it is difficult to obtain in the market

A good source of infrared rays for the spectral range from 1 to 15μ is a thin porcelain tube upon which is wound a fine platinum wire, which is covered with zirconium oxide, alumina, etc., mixed with plaster of Paris. This is heated electrically to incandescence. Formerly the "heater tube" used for preheating the Nernst glower was a useful and easily obtainable source of infrared rays, (Coblentz, Publ. No. 35, Carnegie Inst. of Washington, 1905).

For investigating the infrared of long wave-lengths Rubens (Ann. der Phys. (4), 18, p. 725, 1905; 20, p. 593, 1906) found the Welsbach gas mantle a useful source of radiation.

Other sources are easily suggested, but the ones described are easily obtained and easily kept evenly heated and free from fluctuations in temperature which are caused by air currents.

For calibrating the visible spectrum and the infrared at 1.08μ, a Plücker vacuum tube of helium is very useful. A mercury lamp, also the salts of *Na*, *K*, and *Li* in a cored carbon arc have strong emission lines at 0.76μ to 1.2μ in the infrared.

Standard Spectral Energy Curves.—In certain problems in colorimetry, spectrophotometry, visibility of radiation, etc., it is desirable to know the spectral energy distribution of the visible rays of the light source. In such cases it is desirable to specify the spectral energy distribution in terms of that of a black body at a given temperature, the spectral energy curve of which can be computed and checked radiometrically. In problems not requiring the highest accuracy, a suitable standard of spectral radiation is a cylindrical acetylene flame operated under certain conditions as described by Coblentz, (B. S. Bulletin, 15, p. 639; 1920).

Light Filters.—Numerous filters are available for isolating wide bands of approximately monochromatic light. These may be in the form of salts in solution, of dyed gelatin films, and of colored glasses.

The most important question in connection with the use of a light (thermal radiation) filter is its complete opacity to all rays except those under investigation. This is especially important in problems where the intensity of the stimulus is to be measured radiometrically. Dyes

as a rule are transparent to the infrared at 1μ to 2μ. Hence, when using them as light filters, means must be provided for eliminating the infrared rays from the visual or ultraviolet rays which it is desired to utilize as a stimulus. For example in studying the effect of different colored light rays (obtained by filters) upon plant growth, it is important to eliminate the infrared rays, which would also stimulate growth by raising the temperature of the enclosure. Coblenz (B. S. Bulletin 7, p. 655, 1911; 9, p. 110, 1912) has discussed this question and has described water solutions of cupric chloride, which absorb all of the infrared rays and at the same time maintain a high transmission of visual rays.

In a paper by Coblentz and Kahler (B. S. Bulletin 15, p. 134; 1919) are given a series of filters for obtaining spectral bands at 0.53μ, 0.56μ, 0.77μ, 0.85μ, 2.2μ, 4.4μ, (Bunsen flame), and 8.8μ (residual rays reflected from quartz), useful in spectrophotoelectric work.

Various atlases (e.g., Uhler and Wood, Publ. No. 71, Carnegie Inst. of Washington, 1907; also Smithsonian Physical Tables) describe filters of all sorts for isolating the visual and ultraviolet rays. The ultraviolet and infrared transmission spectra of various glasses are given in B. S. Tech. Papers No. 148 and No. 93, 1920.

BUREAU OF STANDARDS,
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Very Short Sound Waves.—An alternating current of frequency $0.2-2\cdot10^6$ is superposed upon a direct-current arc; the divergent sound issuing from the arc is transformed by a mirror into a parallel beam, which falls upon a grating; the diffracted beam is reconcentrated by a mirror upon a mica vane, the deflection of the suspension indicating the pressure exerted by the sound. From the angle of maximum diffracted intensity, the wave length of the sound is calculated by the usual formula. The least wave length observed was 0.17 mm, apparently the shortest sound waves yet realized. The velocity of propagation of these waves, calculated from their wave length and the ac frequency, is (averaged) 335 m/sec, in good agreement with the values accepted at ordinary acoustic frequencies. [K. Palaiologos. (Berlin, Handelshochschule). ZS. f. Phys. 12, pp. 375–378; 1923.]

KARL K. DARROW

A NEW METHOD OF CRYSTAL ANALYSIS AND THE REFLECTION OF CHARACTERISTIC X-RAYS

By George L. Clark[1] and William Duane

This paper reports researches undertaken for the purpose of studying the crystal structures of secondary valence compounds, such as hydrates, ammines and alkali polyhalides, in the hope of attaining thereby a clearer insight into the nature of the general phenomenon of secondary valence and an explanation of numerous simple relationships between stabilities and atomic and molecular dimensions.[2]

A suitable method of X-ray analysis of complex crystal structures should meet the following requirements. (1) It must be applicable directly to the variable parameter crystal systems—triclinic, monoclinic and orthorhombic—as well as to the others. There is not to be found in the literature a single complete analysis of crystals belonging to these three systems, and very few partial interpretations. Hull[3] has pointed out that the methods of Bragg, Hull-Debye-Scherrer, Laue, Nishikawa-Wyckoff-Dickinson are not now directly adapted to the purpose without complications which have not yet been removed. Bragg,[4] however, has very recently combined his powder-spectrometer method with certain considerations and assumptions as to the symmetry of whole molecules of organic compounds, considered as units in the lattice. In this way he has examined several monoclinic and orthorhombic crystals. A long step must be taken to determine *atomic* effects in complex structures by this method: for, one of the fundamental requirements of a new method of analysis is that it must not depend upon assumptions as to the shape of a cesium tri-iodide *molecule*, for instance, but shall be able to determine the positions and effects of cesium and iodine *atoms*.

(2) Furthermore, the method must be as nearly as possible absolute. It should not depend upon originally assumed structures and numbers of molecules per unit volume, nor upon previous determinations of wave-lengths based upon assumptions, densities, and doubtful distributions of intensities. The well-known "sodium chloride" arrangement has been commonly accepted as correct for that salt and as a standard. Wyckoff[5] claims, however, that not only will this structure, in which the unit cell contains four molecules, agree with the

data, but also others, as, for example, a unit cell containing 24 molecules. Hence for these two cases the wave-lengths would stand in the ratio $\sqrt[3]{4}$ to $\sqrt[3]{24}$ at a given angle θ. It is clear that in order to avoid such an indeterminate process recourse must be taken to a different and more direct method of evaluating wave-lengths, which will in turn determine crystal structures. Again, many attempts to assign absolute and final values to 5 or 6 decimal places to lattice interplanar distances, and hence wave-lengths, depend upon the more or less arbitrary selection from the literature of one of a number of discrepant values of the density of the compound.[6] The absurdity of this has been pointed out by Professor Gregory P. Baxter of Harvard University from his unequalled experience in density determinations of the highest attainable accuracy. Even when impurities and inclusions have been reduced to a minimum the density may not check with the theoretically ideal and, usually, maximum value calculated back from X-ray data. This point is well illustrated by the results obtained with cesium iodide, considered later in this paper. The salt was of atomic weight purity. The density, calculated from the X-ray determination independently of all assumptions and previous values, came out 4.513. Baxter and Wallace[7] found 4.509 for the *same* sample.

(3) Other requirements of a new method are that it should be applicable to either single crystals or powders; be capable of using easily a large range of wave-lengths as required for complicated lattices and great densities, and be sensitive and accurate enough to detect differences in the reflecting powers of closely similar atoms.

In the researches reported in this paper, the following results have been thus far obtained: (1) the development of a new method of crystal analysis to meet as nearly as possible the foregoing requirements; (2) the crystal structure determination of KI, CsI, KI_3, CsI_3, and $CsIBr_2$, respectively simple cubic, body-centered cubic, monoclinic, and the last two orthorhombic; (3) the incidental detection, study and identification of the regular reflection by these crystals of X-rays characteristic of the elements cesium, iodine and bromine contained in them, in addition to the regular reflection of rays characteristic of the target; (4) the separate analysis of the space distributions of cesium and iodine atoms in the same crystal in spite of the fact that the two elements lie so close together in the table of chemical elements; (5) the detection and extended study of the anomalous reflection of characteristic iodine rays by KI, obeying none of the usual laws and, at present, inexplicable upon the basis of prevalent theories;

(6) the incidental test of the validity of the law $n\lambda = 2d \sin \theta$, and the quantum law applied to X-rays $V\lambda = hc/e$ = a universal constant, and (7) experimental light upon such phenomena, possibly, as excitation, orientation, electronic structure, mutual effect of atoms, damping and time lag, and secondary valence.

THE METHOD

The method devised for the study of crystal structures utilizes an ionization spectrometer.[8] The essential parts of the instrument have been fully described in numerous earlier papers by Duane and his collaborators.[9] In most of the experiments the spectrometer table was the one with immeasurably small eccentricity used by Duane, Palmer and Yeh[10] in their measurement of the radiation constant, h. The pyrex glass ionization chamber was 35 cm long and had one end blown very thin for a window. It was completely protected against stray radiation by a heavy lead casing. A potential of 80 volts was applied to the chamber plate. Leaks and surface emf's were rarely encountered, and eliminated and corrected for upon appearance. In the quadrant electrometer a special full-length silver suspension enabled us to attain a sensitiveness of 5 meters' deflection per volt.

The new method employs X-rays belonging to the continuous spectrum, and therefore containing rays of a great variety of wave-lengths, and not the line spectra, of definite wave-lengths. This procedure has certain definite advantages. An ordinary X-ray tube with a tungsten target may be used, and high voltages may be applied to it. More intense X-radiation can be obtained from tungsten than from such chemical elements as rhodium and molybdenum. Further, in some cases it is desirable to employ X-rays of shorter wave-lengths than those in the K series of Rh and Mo, for these shorter rays are more penetrating than the longer ones. As a rule the spectrum between .12 and .80 Å. has been used. Moreover, as will be shown later, in some cases the tungsten tube may be operated at a potential below 69,300 volts, the critical value required for the generation of the K line spectrum of tungsten, so that the reflection spectra from crystals are characteristic of elements in them, provided that the X-ray tube is operated at a voltage above certain critical values. Under certain conditions at a potential above 69,300 volts it has been found possible to produce in the *same* spectrum reflections characteristic of the K-series of the tungsten target and of elements in the crystal which is doing the reflecting.

For high voltages a 500-cycle generator-transformer-kenotron rectifier system has been used, while for potentials below 43,000 volts a lead storage battery has proved of invaluable service, because of its almost perfect steadiness, particularly in that procedure in the method in which wave-lengths are absolutely determined from critical voltages. Voltages have been measured by an electrostatic voltmeter repeatedly calibrated by the measurement of the current flowing through a series of manganin coils of known resistance (approximately 6,000,000 ohms).

The substance to be examined may be in the form of powder or single crystals. Most of the results so far have been obtained with crystals having volumes of .1 to 25 cubic mm. Their small dimensions enabled us to study easily the transmission of X-rays through the crystals, as well as the reflection from surfaces. The large effects and the very satisfactory results which have been obtained from these small crystals are indicated by the data for specific compounds presented in a later section of the paper. Powders have yielded very satisfactory and easily interpreted results for the simpler crystal structures. The extension of their use alone for the study of complex variable parameter crystal systems has not yet been completely accomplished.

In making an analysis the crystal is mounted at the center of the spectrometer so that the axis of the crystal lies parallel to the axis of rotation, and so that the center of the incident beam of rays and the effective reflecting plane of the crystal lie on the axis of rotation. This adjustment is effectively accomplished in the case of the small crystals in the following manner. The slits of the instrument are made fairly narrow, 1 mm or less, and the X-ray tube turned so that the rays that pass through the instrument leave the target almost grazing its surface, thus giving a narrow beam of rays. An image of the narrow slit is produced upon a fluorescent screen. A small crystal in position produces its own shadow in this slit image parallel to the axis of rotation. If the crystal is correctly adjusted, the position of the shadow in the center of the slit image remains unchanged during a rotation of the crystal of 360°. The precision with which the instrument and crystal have been set up is tested in the subsequent analysis of the X-rays reflected on the two sides of the path of the incident beam.

Next the ionization chamber is set so that the line from the axis of rotation to the chamber's slit makes an angle, α, of convenient size (usually about 10°) with the direct beam of rays. The exact determination of the zero position of the spectrometer corresponding to the direct beam will be described in connection with the spectra of

KI. Keeping the ionization chamber angle fixed, the crystal is turned by steps, and the ionization current measured at each step. When a set of parallel planes in the crystal lie at an angle, θ, to the incident beam the planes pick out of the beam X-rays of certain definite wave-lengths, λ, and reflect them into the chamber, as indicated by a marked increase in the ionization current. Evidently the angles between the positions of the crystal that correspond to maximum ionization currents, in other words, between the peaks, are the angles between the crystal planes. The peaks correspond to planes designated as 100, 110, 120, 130, 010, etc. In a cubic crystal major peaks will appear at angles measured from the 100 peak of 90°, 45° (110), 18.37° (130), 26.57° (120), etc. It has been possible, in some of these experiments, to detect and identify reflection from planes at an angle from the 100 planes whose tangent is $\frac{1}{8}$. Obviously, the determination of these interplanar angles gives at once the crystallographic system to which the crystal belongs. The procedure is possible *only* by the use of the general X-radiation.

Before the distance between successive parallel planes can be determined, it is necessary to know the wave-length, λ, of the particular ray which is reflected by the given set of planes at the angle θ. In order to determine λ it is unnecessary to depend upon any previous measurements or assumptions concerning crystal structures, numbers of molecules per unit, lattice interplanar distances, wave-lengths or densities. Use is made of the fact[11] that, according to the quantum law, in order to produce an X-ray of wave-length λ, the voltage, V, applied to the X-ray tube must have a value at least as large as that given by the equation

$$Ve = hc/\lambda, \quad (\text{or } V\lambda = \text{the constant } 12{,}350), \qquad (1)$$

where e is the charge of an electron, h, Planck's action constant, and c, the velocity of light. This application of the quantum law is independent of *a priori* X-ray data except insofar as the most accurate determination of h (6.556×10^{-27}) has been made by using X-rays.[10] The actual experimental determination consists in setting on the peak corresponding to the set of parallel planes for which the distance d is sought, and then lowering the voltage applied to the X-ray tube by steps, while the power is kept constant by increasing the current, until the ionization current disappears. At this critical voltage, V, which may be determined very accurately, if the voltage is constant, as from a storage battery, the longest wave-length which may be reflected from the given set of planes at the given angle is no longer

generated. This value of V substituted in equation 1, gives λ. The value of λ is in turn substituted in the fundamental equation of X-ray reflection

$$n\lambda = 2d \sin \theta, \tag{2}$$

where n, the order, must be 1 for the longest wave-length, λ.

If the specimen to be examined has the form of a powder, a uniform, thin, flat layer of the fine powder, between very thin sheets of mica, is placed at the center of the spectrometer. With the ionization chamber at the angle $\alpha = 2\theta$ as before, the voltage is reduced by steps until the ionization current vanishes. The voltage at this point can no longer produce the longest X-rays reflected at the angle, θ, by the powder. This maximum wave-length corresponds to $n = 1$ in equation (2) and to the greatest distance d between successive planes in the crystal that are alike. In addition to these planes, however, all other planes reflect X-rays due to the random orientation of powder grains. Consequently, the ionization current voltage curve shows, in addition to the point where the ionization current vanishes, several well-marked places where the curvature changes abruptly.[12] These breaks in the curve correspond to the critical voltages at which the rays reflected from other crystal planes cease to be produced. Equations (1) and (2) determine the wave-lengths and interplanar distances as before. For a simple cubic lattice such as that of KI the 3 most sharply determined voltages are in the ratio $1 : \sqrt{2} : \sqrt{3}$, corresponding, respectively, to the 100, 110 and 111 planes. It has been found in these experiments with powders that even the large number of parameters in an orthorhombic crystal are clearly defined by changes in slope of the voltage curve.

In addition to the above, the following procedure has been found to furnish important data. This consists in determining the spectrum of the reflection from a set of parallel planes in question, for example, the 100 planes, as it was located in the first procedure in the analysis, and then changing by steps the angles of both the crystal and the ionization chamber, moving the latter at twice the rate of the former. Instead of finding then a series of peaks corresponding to different sets of planes, the reflection from the 100 planes alone is analyzed. By use of this procedure it has been discovered that a crystal reflects not only the rays belonging to the line spectrum of the tungsten target (provided that a voltage above 69,300 volts is applied) but also rays produced by excitation of atoms within the crystal and characteristic of the chemical elements which have combined to form the compound.

The complete new method of analysis in its essential features comprises the three procedures just outlined: (1) the determination of the interplanar angles, and hence lattice classification; (2) the independent and direct evaluation of wave-lengths and interplanar distances by the experimental determination of critical voltages; and (3) the analysis of the reflection from a given set of planes, which permits evidence of the space distribution of each kind of atoms. Certain other auxiliary procedures, such as the relative absorptions of primary and secondary X-rays in metals, will be considered in connection with the discussion of specific crystals. The experimental results obtained by the foregoing method for crystals of each of five alkali halides and polyhalides are presented in the following sections.

THE CRYSTAL STRUCTURE OF POTASSIUM IODIDE, KI

Single small crystals and powders of potassium iodide have been used in this work to develop and test the method just described. The structure of this salt has been previously investigated by Bragg,[13] Hull,[14] Davey,[15] and Wyckoff.[16] All agree that it is simple cubic (each element alone face-centered), a conclusion verified by the results of our new method of analysis. Values of d, the distance between successive planes have been found as follows: Bragg, 3.55; Hull, 3.55; Davey, 3.520 and 3.525; Wyckoff, 3.555; Clark and Duane, 3.532 to 3.535×10^{-8} cm. Calculating the density from our best value, 3.532×10^{-8} cm, we find 3.112 as compared with Baxter's direct measurement of the density, 3.114.[17] The sample used in our X-ray analysis was probably of greater purity than any used in previous work, though perhaps a little less pure than the "atomic weight" sample of cesium iodide, the analysis of which will be described later.

Since the results have already been published in brief form[8] for potassium iodide, the experimental data will be presented in tabular form only. The various columns of Table 1 contain the following data: 1. the number of the crystal; 2. angle of incidence, θ, ($\frac{1}{2}$ ionization chamber angle); 3. spectrometer reading of crystal table corresponding to peaks; 4. angle ϕ between a given peak produced by reflection from certain planes and the 100 peak; 5. the angle ϕ calculated by solid geometry for a cubic lattice; 6. designation of planes corresponding to peaks; 7. the experimentally determined critical voltage for a given peak; 8. the wave-length calculated from the critical voltage by means of equation (1); 9. the value of d, calculated by equation (2).

For *powdered* potassium iodide the curve obtained by plotting the ionization currents as functions of the voltage applied to the tube showed two well-marked points of inflection at 37,600 and 31,010 volts, in addition to the point at which the current vanished, at 21,740 volts. These voltages are, to within a very small error, in the ratio of $\sqrt{3} : \sqrt{2} : 1$, respectively. The corresponding wave-lengths calculated from

TABLE 1. *Interplanar Angles, Critical Voltages, Wave-lengths, and Distances for KI Crystals.*

No.	θ	Spectrometer Reading.	ϕ Exptl.	ϕ Cubic	Planes	V	λ	$d \times 10^8$ cm
1	5.51°	40.94°			100	18 600	.664	3.535
		130.94°	90°	90°	010			
		−4.02°	44.96°	45°	110	26 310	.470	2.495
		14.42°	26.52°	26.57°	120			
		22.57°	18.37°	18.43°	130			
2	5.05°	41.80°			100	19 420	.622	3.532
		−3.15°	44.95°	45°	110	27 460	.4396	2.497
		15.28°	26.52°	26.57°	120			
		23.40°	18.40°	18.43°	130			
3	12° 30′	140° 12.5′			100	8 125	1.52	3.532
		126° 10′	14° 2.5′	14° 24′	140			
		121° 45′	18° 27.5′	18° 25.8′	130			
4	15°	137° 50′			100			
		130° 45′	7° 5′	7° 7.5′	180			
		129° 40′	8° 10′	8° 8′	170			
		128° 10′	9° 40′	9° 29′	160 ?			
		123° 45′	14° 5′	14° 2.4′	140			
		119° 25′	18° 25′	18° 25.8′	130			
5	17° 30′	135° 20′			100			
		128° 13′	7° 7′	7° 7.5′	180			
		127° 12′	8° 8′	8° 8′	170			
		125° 50′	9° 30′	9° 29′	160			
		124° 4′	11° 16′	11° 18′	150			
		121° 17′	14° 3′	14° 2.4′	140			
		117° 55′	18° 25′	18° 25.8′	130			

equation (1) equal .5424, .3982 and .1327 Å. The angle $\theta = 4.51°$. Hence the values of d from equation (2) are 3.534 (100) 2.496 (110), and 2.041×10^{-8} cm (111). These are in the ratios required for a cubic lattice, and furthermore, accurately check the results obtained with single crystals. A typical *KI* powder voltage curve is shown in the preliminary note.[8]

THE NORMAL REFLECTION BY A CRYSTAL OF KI OF X-RAYS CHARACTERISTIC OF THE IODINE ATOMS IN THE CRYSTAL

The spectrum of the 100 planes of *KI* shown in Fig. 1 comprises a series of well-defined peaks, unsymmetrical in shape and hence different from the peaks obtained for *different* sets of planes in the determination of interplanar angles (see reference 8). These peaks appear always when the voltage on the X-ray tube lies above 33,000 volts. They cannot be due to reflection of the *K* series line spectrum of the tungsten target, since its generation requires more than 69,300 volts. For the spectrum in Fig. 1 we used 62,000 volts.

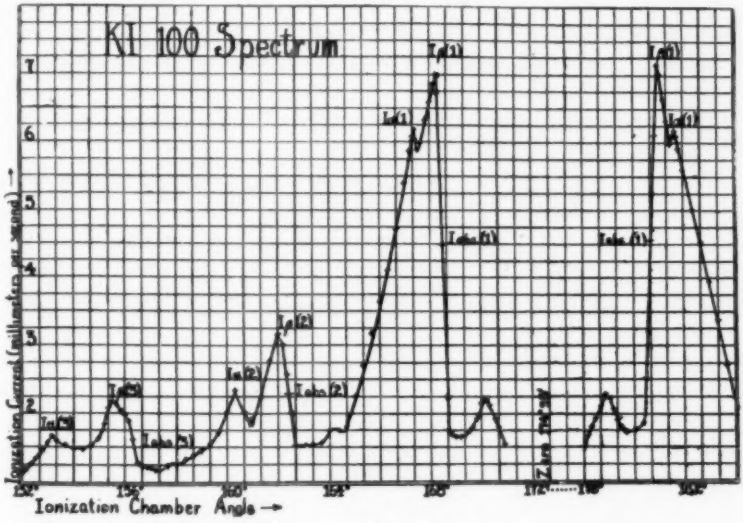

FIG. 1. *Characteristic iodine spectrum reflected by 100 planes of KI.*

A complete spectrum in reality shows two series of peaks, one on each side of the zero; i.e., the angular reading of the spectrometer at which the direct X-ray beam enters the ionization chamber. One series may be considered, therefore, as the mirror image of the other. As a matter of fact, the most accurate method for determining the exact zero point from which all angles are measured consists in finding the point midway between the angular readings corresponding to the same part of the same peak as it occurs on either side of the direct beam zone.

Near the zero appears a small, peak-like hump. The angle at which the curve rises depends only upon the voltage; hence the hump repre-

sents the *general* radiation from the target. From the general radiation curve rises a very tall peak at an angle slightly greater than 3°. This appears when the potential has a value above 33,000 volts, and always at the same angle. It is characterized by a sharp absorption drop on the short wave-length (smaller angle) side, a peak at the top of this steep straight line, and a smaller, symmetrically shaped though incompletely separated, peak on the long wave-length side. Obviously, identification and explanation of this complex peak is possible only with a knowledge of the wave-lengths. By means of the new critical voltage method these wave-lengths corresponding to the center of the absorption drop, the higher and the lower peaks were determined in these experiments. The critical voltages in several separate determinations closely approximated 28,250, 31,500 and 33,000 volts, respectively. The corresponding wave-lengths equal .352, .388 and .437 Å. These agree with the known values[17] of the critical absorption, the K_β and the K_α wave-lengths of iodine.

The other peaks in the spectrum decrease in intensity with increase in the angle. These smaller peaks represent the higher order reflections of the same characteristic iodine radiations observed in the case of the first tall peak. This fact we checked both by the angle and by the critical voltage measurement of the wave-length. A summary of several different crystals and determinations of the spectrum of the 100 planes of *KI* appears in Table 2.

The experimental results summarized in Table 2 show not only that the spectrum peaks correspond to the line spectrum of iodine, and that different crystals under different experimental conditions produce results identical within experimental error, but also that the value of d obtained from the characteristic wave-lengths at the particular angles at which the various order reflections appear, coincides with that calculated from wave-lengths in the continuous X-ray spectrum. In one experiment at an angle, θ, of 5.51° we found the critical voltage to be 18,600 volts, corresponding to $\lambda = .6642$ Å., which is a wave-length in the continuous spectrum. The coincidence in the values of d calculated in these two ways proves that the reflection by the *KI* crystal of X-rays characteristic of the iodine atoms in it is regular in the sense that it obeys the law $n\lambda = 2d \sin \theta$. The detection and identification of this entire secondary phenomenon have not been accomplished heretofore.

We obtained further interesting confirmation that the spectra are characteristic of iodine from one of the experiments with the 110 planes, and with a much higher voltage applied to the tube. *Both* the regular

TABLE 2. *Analysis of the 100 Planes of KI.*

No.	Spectrometer Reading. (1)		θ	Critical Voltage (V)	λ from V	Characteristic of		d
1	36. 9°	(C.T.)	0°					
	39.94°		3.04°	33 000	.374	I_{abs}	(1)	3.532
	40.05°		3.15°	31 840	.388	$I\beta$	(1)	3.532
	40.45°		3.55°	28 400	.435	$I\alpha$	(1)	3.532
	42.41°		5.51°	18 600	.6642			3.534
2	8.69°		0°					
	11.73°		3.04°			I_{abs}	(1)	3.532
	11.84°		3.15°			$I\beta$	(1)	3.532
	12.24		3.55°			$I\alpha$	(1)	3.532
3	174° 35′	(I.C.)	0°	(Cf. Fig. 1)				
	168° 30′	Right	3° 2.5′	33 000	.374	I_{abs}	(1)	3.532
	168° 15′		3° 10′	31 840	.388	$I\beta$	(1)	3.532
	167° 25′		3° 35′	28 400	.435	$I\alpha$	(1)	3.532
	162° 25′		6° 5′	33 000	.374	I_{abs}	(2)	3.532
	162° 0′		6° 18′	31 500	.390	$I\beta$	(2)	3.54
	160° 20′		7° 7.5′	28 250	.437	$I\alpha$	(2)	3.525
	156° 21′		9° 7′			I_{abs}	(3)	3.538
	155° 30′		9° 32′			$I\beta$	(3)	3.532
	153° 5′		10° 45′			$I\alpha$	(3)	3.532
	180° 40′	Left	3° 2.5′	33 000	.374	I_{abs}	(1)	3.532
	180° 55′		3° 10′	31 850	.388	$I\beta$	(1)	3.532
	181° 40′		3° 32.5′	28 250	.437	$I\alpha$	(1)	3.532
4	174° 15′	(I.C.)	0°					
	168° 10′	Right	3° 2.5′			I_{abs}	(1)	3.532
	167° 57′		3° 9′			$I\beta$	(1)	3.532
	167° 15′		3° 30′			$I\alpha$	(1)	3.534
	162° 0′		6° 7.5′			I_{abs}	(2)	3.532
	161° 37′		6° 19′			$I\beta$	(2)	3.535
	160° 15′		7° 0′			$I\alpha$	(2)	3.534
	180° 17′	Left	3° 1′			I_{abs}	(1)	3.535
	180° 32′		3° 8.5′			$I\beta$	(1)	3.533
	181° 20′		3° 32.5′			$I\alpha$	(1)	3.532
5	174° 8′	(I.C.)	0°					
	168° 2′	Right	3° 3′			I_{abs}	(1)	3.532
	167° 48′		3° 10′			$I\beta$	(1)	3.532
	167° 0′		3° 34′			$I\alpha$	(1)	3.531
	180° 13′	Left	3° 2.5′			I_{abs}	(1)	3.532
	180° 27.5′		3° 9.7′			$I\beta$	(1)	3.532
	181° 8′		3° 30′			$I\alpha$	(1)	3.534

(1) Two spectrometers have been used in different experiments. C.T. and I.C. refer to crystal table and ionization chamber, respectively.

reflection of the line spectrum of tungsten from the target and the reflection of rays characteristic of iodine in the crystal appeared as shown in Fig. 2. The determination of the value of d_{110}, as presented in Table 1, depended upon the following data: $\theta = 5° 30'$, critical voltage = 26,310 volts, and $\lambda = .470$ Å., the latter a wave-length in the continuous X-ray spectrum; hence, $d_{110} = 2.495 \times 10^{-8}$ cm, which stands to within a very small fraction of one percent in the ratio $1/\sqrt{2}$ with the average value from more than 10 determinations of d_{100}, namely, 3.532×10^{-8} cm. The wave-lengths of the peaks in Fig. 2 may be determined either by the approved critical voltage method if a storage

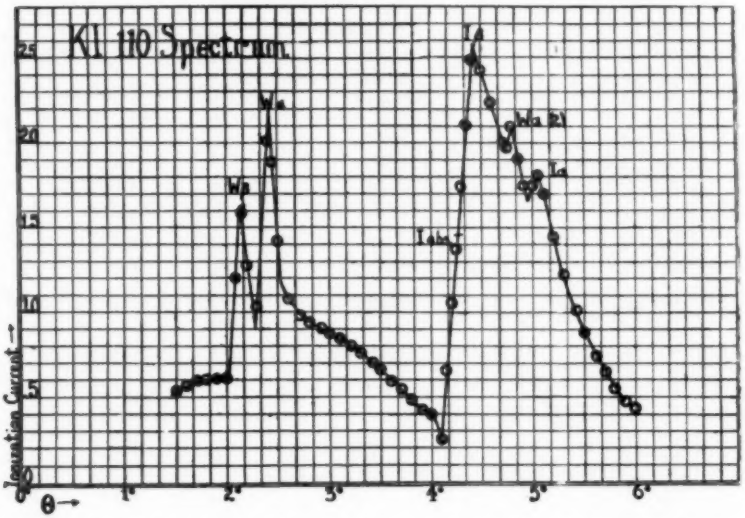

FIG. 2. *Characteristic tungsten and iodine spectra reflected by 110 planes of KI.*

battery of sufficiently high potential (above 69,300 volts) is available, or by calculation by means of the equation $n\lambda = 2d \sin \theta$ from a well-established value of d. Adopting the latter procedure in Table 3, the first column gives the crystal table angle, the second the angle, θ, the third, λ, calculated upon the basis that $d_{110} = 2.495 \times 10^{-8}$ cm, the fourth the true, known wave-length[18] of the line in the K series spectrum of the element tabulated in the fifth column.

In addition to the check in the values of wave-lengths, and hence of d_{110}, this mixed spectrum furnishes two interesting comparisons: (1)

the characteristic iodine reflections are more intense than the tungsten lines; and (2) whereas the α-peak is always higher than the β-peak for the regularly reflected target line spectrum, the reverse holds true for rays characteristic of elements in the crystal. In all cases so far investigated, both for iodine and for other elements in crystals, the β-peak always exceeds in height the α-peak.

TABLE 3. *The Analysis of the Spectrum of the 110 Planes of KI.* (*High Voltage Applied to X-ray Tube.*)

Crystal Table Angle	θ	λ (calc'd.)	λ (true)	Element and K series line
13° 37′	0°			
15° 45′	2° 8′	.185	.1842	Wβ
16 2′	2° 25′	.210	.211	Wα
17° 54′	4° 17′	.374	.3737	I_{abs}
18° 3′	4° 26′	.387	.388	Iβ
18° 25′	4° 48′	.420	2×.211	Wα (2nd)
18° 40′	5° 3′	.439	.437	Iα

The reflection of characteristic X-rays seems to be reasonably well explained by the assumption that a single primary X-ray excites secondary characteristic X-rays in a *lot* of atoms with a certain time lag which is approximately the same for all the atoms of one kind (see reference 8). It is not necessary to assume that the primary ray has wave-lengths, but only that it must have been produced by a voltage above certain critical values. If the secondary rays have wave-lengths, they will interfere and produce beams in the required directions. This point of view, however, does not appear to be compatible with the law of the conservation of energy applied to the processes going on in individual atoms.

If, contrary to the present interpretation of certain experimental results, a primary X-ray produced a secondary, characteristic wave train travelling substantially in the same direction as the primary beam, this secondary wave train might be reflected from atoms further along in its path and produce the observed phenomenon. If spherical characteristic wave trains, spreading out from atoms in the crystal and reflected from other atoms, produced the effects, then the direction of the reflected beam ought not to depend upon the angle of incidence of the primary X-ray, which it does, according to our experiments.

It is interesting to note that the complete analysis of *KI* furnishes another example of the fact that a *quantum* equation and an *interference*

equation hold simultaneously in the process of the reflection of X-rays by crystals, even though quantum and interference mechanisms appear to be incompatible.

THE ABNORMAL REFLECTION BY A CRYSTAL OF KI OF X-RAYS CHARACTERISTIC OF IODINE IN IT

In the experimental results presented in the preceding section we found that *KI* crystals reflect, according to the law $n\lambda = 2d \sin \theta$, the *K*-series line spectrum of iodine produced by the excitation of the atoms in the crystal. In addition to this normal reflection we have observed in these experiments that reflection of the characteristic iodine rays may also take place in an entirely anomalous fashion. In the original determination of angles between reflecting planes in *KI*, a peak only slightly lower than the peaks corresponding to the 100 and 110 planes, appeared unexpectedly at an angle of 17° 38′ from the 100 peak (the ionization chamber being at an angle of 10°). This peak does not correspond to any planes within the crystal with simple indices, since the 130 planes are at an angle of 18° 25.8′ from the 100 planes. We have investigated this peak in considerable detail, with the results outlined in the following paragraphs.

1. The wave-length of the peak as originally observed was determined by the critical voltage method. The ionization current vanished at 30,000 volts, corresponding to a wave-length of .412 Å., which is a good mean of the wave-lengths of the β and α lines in the *K* series of iodine, respectively .388 and .437 Å.

2. The peak does not appear when the X-ray tube is operated below 33,000 volts, the critical voltage for the production of characteristic iodine wave-lengths, but it is just observable at 33,500 volts. The fact that the ionization current in the critical voltage experiment became zero at 30,000 volts, rather than at 33,000 volts, means that it vanishes only when the voltage becomes insufficient to produce an X-ray in the continuous spectrum of equal wave-length to that of the characteristic line.

3. We have observed this X-peak reflection from four different crystals of *KI* under entirely different circumstances, including different spectrometers. At an ionization chamber angle (α) of 10° the peak appeared in every case at the angle 17° 38′ from the 100 peak.

4. The X-peak occurs symmetrically on both sides of the 100 peak and 8 times in a crystal rotation of 360°. It is produced, therefore, either when the primary beam is transmitted through the thinnest part

of the crystal or when it is largely reflected from the broader surfaces, though more prominent and best defined in the case of transmission.

5. The peak has been investigated and its appearance identified at angles, α, from 2° to 30°. Its angular distance from the 100 peak changes and depends in a peculiar way upon the angle of incidence. For example, at $\alpha = 2°$, it is at an angle, ϕ, of 19° 38′ on both sides of the 100 peak; at $\alpha = 4°$, $\phi = 19° 8'$; at $\alpha = 10°$, $\phi = 17° 38'$, etc. The value of the angle ϕ decreases regularly by 15′ with each increase in α of 1°, up to $\alpha = 20°$ when $\phi = 15° 8'$. Thus, while in the regular reflection from 100 and 130 planes the crystal angle changes 30′ for every 1° change in α, the X-peak changes on one side 15′ and on the other 45′,

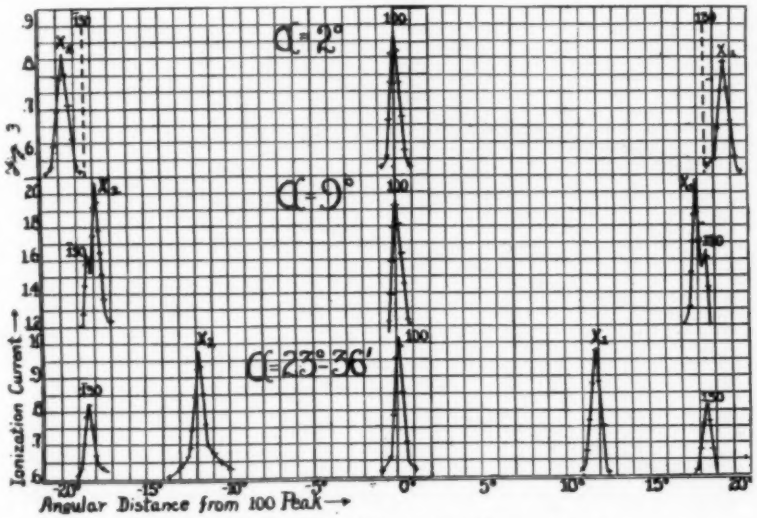

FIG. 3. *Relative positions of X-peaks for different values of* α.

thereby retaining symmetry of position with respect to the 100 peak. This anomalous change in position shows that it cannot be due to regular reflection from any given set of parallel planes. The X-peaks are distinctly separate from the 130 peaks at small values of α, approach them with increase in angle, coincide with them at $\alpha = 6° 25'$ (which curiously happens to be the angle 2θ at which the first order characteristic emission peak of iodine appears in the spectrum of the 100 planes of KI), and again become separate at larger angles. Figures illustrating the relative positions of the 100,130 and X-peaks have been published for $\alpha = 11°$[8], and for $\alpha = 16°$ & $20°$[19]. Fig. 3 in this

paper shows the experimentally determined peaks at $\alpha = 2°$, 9° and 23° 36′.

The constant rate of change with which the X-peaks approach the 100 peaks does not continue above $\alpha = 20°$. At $\alpha = 25°$ the angle ϕ is 10° 22′ instead of 13° 53′ as would be the case if the rate were constant. At $\alpha = 30°$, $\phi = 4°$; at 35° the X-peaks do not appear. The figure obtained by plotting α against the crystal angle for the X-peaks shows a straight line from 2° to 20° followed by a sharp change in slope and another straight line, which upon extrapolation cuts the straight line representing the change in crystal angle with α (1 : 2) for the 100 peaks. Fig. 4 presents, at a glance, these relationships.

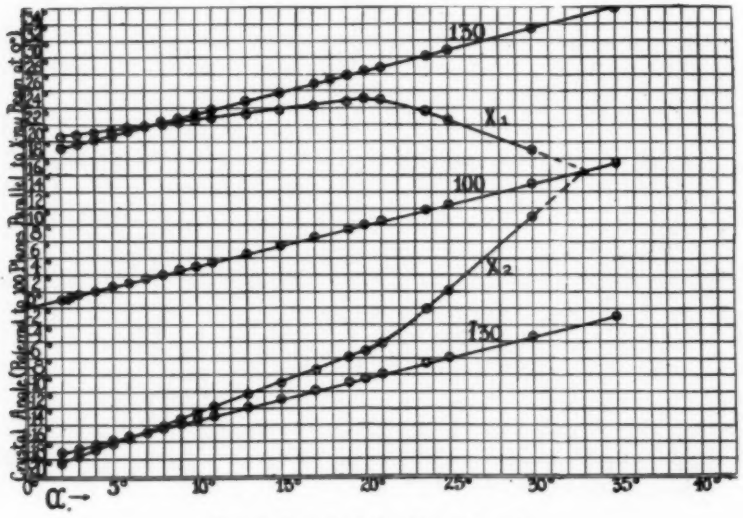

FIG. 4. *General relationships of X-peaks.*

Fig. 4 discloses the fact that when the crystal angle is zero, or in other words, when the incident X-ray beam is parallel to the 100 planes, the X-radiation enters the ionization chamber at an angle of about 23° 40′. We have verified this in the following ways: (1) by setting the crystal at 0° for the 100 planes and moving the ionization chamber, a well-defined peak appeared at 23° 36′ in one experiment and 23° 40′ in another; (2) by setting the crystal so that the 100 planes would reflect into the ionization chamber at 23° 40′ and then finding the angle (about 11° 50′ indicated by the figure) through which the crystal must be

turned to enable reflection of the X-radiation; and (3) by taking a Laue photograph (reproduced in Fig. 5) of the crystal reflection when crystal axis lay parallel to the X-ray beam. The film placed 2.5 cm behind the crystal, registered the reflected rays and the direct X-ray beam passing through a small hole. An excellent photograph was obtained showing clearly spots about 1 cm from the central image of the direct beam, and directly in a line with it to the right, to the left, above and below. Using this approximate data, the calculation of the angle whose sine is 1/2.5 or .4 gives 23° 36′. The exposure was not long enough to detect regular reflections from the various crystal planes as in Laue's classical experiments.

FIG. 5. *Photograph showing reflection of characteristic X-rays*

Corresponding to this X-peak position for the 100 planes parallel to the incident beam, there is an X-peak for the same angle, $\alpha = 23°$ 40′, when the crystal angle is 23° 40′ also. In this case the 100 planes lie parallel to the reflected ray.

6. The preceding facts prove that the reflection of this X-peak radiation does not obey the laws that the angle of reflection equals the angle of incidence for any one plane in the crystal, and that $n\lambda = 2d \sin \theta$. This anomaly receives further verication from the results of the experimental determination of the wave-lengths by the critical voltage method. For, entirely independently of the angle, the wave-length *remains constant*. The critical voltage for a large number of determinations at different angles between 2° and 30° had the average value 31,300, (see reference 19) corresponding to a wave-length of .392 Å. This wave-length exceeds only slightly the characteristic K_β wave-length of iodine (.388 Å.). In every case the values lay between the K_β and the K_α wave-lengths. One single value for all the determinations can scarcely be expected, inasmuch as it is practically impossible to set the spectrometer on exactly the same portion of each of a large number of peaks.

The results of more than 40 experiments on angles, critical voltages, etc., appear in Table 4. In this table the arbitrary spectrometer readings for the position of the ionization chamber when the direct beam entered (174° 10′) and of the crystal table when the 100 planes were parallel to the beam (64° 18′) are both put at O and all other readings referred to them. With the exception of the first and last columns the data refer to crystal angles.

7. Experiments to determine the ratio of the absorption in copper of the primary X-ray beam to that of the secondary characteristic iodine X-radiation, have been made. There appears to be greater absorption of the secondary characteristic rays than of the primary beam. The latter must, therefore, contain rays of shorter wave-lengths than the former, which agrees with the results described above.

8. This X-peak reflection has not been explained by any simple analysis. The direction in which the secondary ray travels from an atom depends in a very complicated fashion upon the angle of incidence of the primary beam and upon the positions of neighboring atoms. The phenomenon requires no specific wave-length in the primary beam, but only that the X-ray tube shall be operated above 33,000 volts. McKeehan[20] has attempted an explanation of the X-peaks of *KI*, since the announcement of their discovery in a preliminary note.[8] Unfortunately, his analysis proves entirely inadequate to explain the numerical results and the peculiar variations in the positions of the X-peaks. Furthermore, his equations contain the wave-lengths of the incident beam of rays, whereas the position or production of the X-peaks do not appear to depend upon the voltage applied to the X-ray tube, provided that the voltage is above the critical value, 33,000 volts. In other words, the X-peaks do not depend upon the wave-lengths of the incident beam, provided only that they are shorter than the critical absorption wave-length of iodine.

THE STRUCTURE OF POTASSIUM TRI-IODIDE, KI_3

With the new method of crystal structure analysis established in its fundamental features by the study of *KI*, its extension to the more complex structures of secondary valence compounds followed. It seemed logical to select potassium tri-iodide, not only because of its close relationship as a polyhalide to *KI*, but also because of its great chemical interest and importance in such matters as iodometric analysis etc.

TABLE 4. *Experimental Data for X-Peaks.*

a	Angle 100	Angle 130	Angle 130	Angle 100 to 130	Angle X_1	Angle X_2	Av. Angle 100 to X	Critical Voltage
2°	1°				20° 38′	−18° 37′	19° 38′	31 600 31 800
3°	1° 30′				20° 53′	−17° 53′	19° 23′	
4°	2°				21° 8′	−17° 7′	19° 8′	
5°	2° 30′				21° 23′	−16° 23′	18° 53′	
6° 25′	3° 12.5′			18° 25.8′	21° 38.5′	−15° 14′	18° 26′	31 500
7°	3° 30′	21° 42′		18° 12′?	21° 53′	−14° 53.5′	18° 23′	31 000
9°	4° 30′	22° 48′		18° 18′?	22° 23′	−13° 23′	17° 53′	
10°	5°	23° 26′	−13° 26′	18° 26′	22° 38′	−12° 38′	17° 38′	30 800 31 650
								31 500 31 800
11°	5° 30′	23° 54′	−12° 54′	18° 24′	22° 53′	−11° 54′	17° 23′	30 800
13°	6° 30′	24° 54′	−11° 54′	18° 24′	23° 23′	−10° 23′	16° 53′	
15°	7° 30′	25° 55′	−10° 55′	18° 25′	23° 53′	− 8° 54′	16° 23′	
16°	8°	26° 25′	−10° 25′	18° 25′	24° 8′	− 8° 7′	16° 8′	30 800
17°	8° 30′	26° 55′	− 9° 55′	18° 25′	24° 22′	− 7° 23′	15° 53′	
19°	9° 30′	27° 55′	− 8° 54′	18° 24.5′	24° 53′	− 5° 53′	15° 23′	
20°	10°	28° 26′	− 8° 24′	18° 25′	25° 8′	− 5° 8′	15° 8′	31 800 (2)
21°	10° 30′				25° 0′	− 4° 0′	14° 30′	
23° 40′	11° 50′				23° 40′	0°	11° 50′	
25°	12° 30′	20° 55′	− 5° 55′	18° 25′	22° 54′	+ 2° 8′	10° 22′	31 000
30°	15°	33° 25′	− 3° 25′	18° 25′	19° 0′	+11° 0′	4° 0′	
35°	17° 30′	35° 55′	− 0° 55′	18° 25′	.....	.....	.....	

Splendid crystals of convenient size and thickness for transmission experiments separated after very slow spontaneous evaporation *in vacuo* from a strong aqueous solution containing theoretical quantities of KI and iodine. Without a very careful control of the evaporation, a mud of indefinite composition precipitated. Since the vapor pressure of iodine from the compound reaches 760 mm in an enclosed space at 146°C, it became necessary during the analysis to protect the crystal against rapid loss of iodine by enclosing it in a very thin glass bulb mounted on the crystal table.

The analysis proceeded in exactly the same way as outlined for KI. In the determination of the angles between planes, peak reflections occurred at angles of almost 90° and 45° from the peak for the 100 reflections. The angular reading for the 100 peak was 45° 48′, and for the 100 peak 0° 30′. This slight departure of about 18′ from perfect cubic symmetry verifies the discovery by Wells and Penfield in goniometric measurements that one of the axes is slightly inclined to the plane containing the other two at right angles. The experiments indicate, therefore, a cube slightly distorted into a monoclinic prism. The critical voltage for the 100 peak produced by transmission through the crystal approximated 11,300 volts at an angle, θ, of 6° 45′, corresponding to the wave-length 1.09Å. Substituting this value in the equation $\lambda = 2d \sin \theta$, gives $d_{100} = 4.68 \times 10^{-8}$ cm. The number of molecules per unit, calculated from $m = \rho\ d^3/Ww$, where ρ, the density, is 3.398, W, the molecular weight, is 419.86 and w, the weight of the hydrogen atom, is 1.663×10^{-24}, comes out .51 or ½ molecule. Hence the original unit cube of KI with $d = 3.532$ has expanded to a very slightly distorted cube with an edge length of 4.68×10^{-8} cm and with an extra atom of iodine at or very near the center.

Again, as in the case of KI, the spectrum of the reflection furnished striking confirmations and additions. The KI_3 spectrum duplicates that of KI in that it is characteristic of iodine. The spectra of the former for the 100 and 010 planes shows the iodine peaks at almost exactly the same angles. A well-defined first order peak at the top of the sharp absorption drop appears at 2° 21′ and another, less prominent and incompletely separated, at 2° 39′. As in the case of KI, the center of the absorption drop, the higher and the lower peaks have wave-lengths corresponding, respectively, to the critical absorption, the K_β and the K_α lines of iodine. The same reflections repeat themselves through 4 orders. Calculating d from $.388 = 2d \sin (2° 21′)$ and $.437 = 2d \sin (2° 39′)$ gives the value 4.70×10^{-8} cm. Considering that

the calculation from a wave-length in the continuous spectrum involved an unusually long wave-length, 1.09Å., the value of d agrees remarkably well with that calculated from the characteristic iodine wave-lengths.

THE STRUCTURE OF CESIUM IODIDE, CsI

Cesium iodide of atomic weight purity was kindly furnished for this work by Professor G. P. Baxter. The procedure for the analysis did not differ from that applied in the type case of *KI*. One of the small 6-sided crystals, not over .1 mm in volume, was set up. The peaks representing reflection from different planes appear similar to those for *KI* shown in Fig. 1 in our former note.[8] The 100 and the 110 planes, at $-1.76°$ and $43.24°$ respectively, lie at an angle of exactly 45° apart. Hence the space lattice is immediately designated as cubic. Three other peaks corresponding to different sets of planes of major importance appear in Table 5.

TABLE 5. *Interplanar Angles of CsI*

Angle Reading	Angle with 100 Planes	Planes	Angle with 100 Planes (calc'd.)
−1.76°		100	
43.24°	45°	110	45°
31.93°	33.69°	230	33.684°
24.81°	26.57°	120	26.56°
16.70°	18.46°	130	18.43°

The voltage curves obtained in the experimental determination of the wave-lengths corresponding to the 100 and 110 peaks appear similar to the curves for *KI* shown in Figure 2 in our former note.[8] At the angle $\theta = 5°.56$, the critical voltages, 29,100 and 20,580 volts, respectively, stand in the ratio $1.414 : 1$ ($\sqrt{2} = 1.4142$). We found the opposite ratio was true for *KI*, and hence designate the lattice of *CsI* as body-centered cubic. Since successive planes containing cesium and iodine have so nearly the same reflecting power, the use of wave-lengths in the continuous spectrum does not permit distinction between them. Hence d_{100} as calculated is only ½ the edge length of the unit cube containing 1 molecule of *CsI*, or 2.281×10^{-8} cm. The distance between planes containing like atoms equals, therefore, 4.562×10^{-8} cm, which is $\sqrt{2}$ times the distance between the 110 planes, 3.226×10^{-8} cm as determined in a separate experiment.

An experiment on the 100 spectrum gave what has proved to be a very important result. The first order spectrum peak appeared more

complicated than that, obtained for KI and KI_3, characteristic of iodine. The center of the absorption drop came at 2.17°, the tallest peak at the top of it at 2.22°, and 3 incompletely separated peaks on the long wave-length side of the great peak in which all coalesce at 2.45°, 2.53°, and 2.75°. Assigning to these points, respectively, the wave-lengths .344(Cs_{abs}), .352(Cs_β), .388(I_β), .400 (Cs_α), and .437 (I_α), d comes out within .1% of 4.56×10^{-8} cm in every case. The very significant fact thus develops that rays characteristic of ***both cesium and iodine*** are reflected by the CsI crystal, and that in spite of the close simularity in wave-lengths, it is possible to distinguish between planes containing cesium and those containing iodine even in the first order of the doubly characteristic reflection spectrum. The separations appear complete in the higher orders. The analyses of CsI_3 and $CsIBr_2$ further verify these facts.

As already pointed out in the first part of the paper, the density of CsI calculated from $d_{100}=4.562\times10^{-8}$ cm is 4.513, as compared with the experimental value of 4.509, determined by Baxter and Wallace[7] on the same sample. Considering the undoubted purity of the crystal, the extraordinary care used in the analysis, and the very satisfactory checks, the value 4.562×10^{-8} cm constitutes as nearly an absolute value as any ever determined. Davey[15] has calculated the value 4.558 and Wyckoff[16] the value 4.55×10^{-8} cm from powder photographs and comparison with data for sodium chloride.

THE STRUCTURE OF CESIUM TRI-IODIDE, CsI_3

Cesium tri-iodide, the most stable of the alkali polyhalides, is well adapted to the study of complex lattice structures and of secondary valence by the determination of the change in structure undergone by CsI when it combines with a molecule of I_2 by means of secondary valence forces. Only one of the polyhalides, $CsICl_2$, has been subjected to X-ray analysis prior to our own investigations. Wyckoff, in a partial analysis, found the crystals rhombohedral hexagonal.

Crystals of CsI_3 were prepared following the original directions of Wells and Penfield. Excellent crystals of definite composition resulted by dissolving 1 part of CsI in 10 parts of hot water and adding only ¼ the calculated quantity of iodine. A single perfect crystal about 1 cm long, 2 mm broad and .2 mm thick served throughout the first analysis. Subsequent recrystallizations never produced specimens as broad as the first one, but in all other respects, they gave the same results.

The crystal was oriented on the spectrometer with the greatest length parallel to the slits. This set-up enabled us to study the 100 and 010 planes. Experiments with the 001 planes necessitated a new adjustment with the crystal on its side. The shape of the crystal with brachy- and macro-pinacoids both developed as faces suggested the orthorhombic system. To confirm this we determined the interplanar angles in the usual way. Exactly at 90° from the setting of the 100 peak, another peak representing planes of maximum reflecting power appeared (010), but at 45° no marked reflection occurred. Instead, a reflection of major importance produced a peak at an angle of 34.31° from the 100 setting. That this represents reflection from the 110 planes was proven by determining the positions of the 120,130, and 430 planes as identified in Table 6.

TABLE 6. *Interplanar Angles of CsI_3 (Referred to 100 Peak)*

Angle Reading	Angle with 100 Planes	Planes	Angle Calculated
46.48°	0°	100	
136.48°	90°	010	
12.17°	34.32°	110	
27.62°	18.86°	120	18.83°
33.64°	12.84°	130	12.82°
4.00°	42.48°	430	42.42°

These measurements, together with similar ones relating to the 010 and 001 planes, indicate that the bounding planes of the unit crystal cell are rectangles. Hence the face diagonals will not bisect 90° into two 45° angles.

In the course of the analysis it became apparent that in a complex crystal such as CsI_3 in which parallel planes might not be alike or equally spaced, only the complete spectra of the reflections from 100,010 and 001 planes would furnish data requisite for satisfactory interpretation. Proceeding in the manner described for KI, we obtained the spectrum for the 100 planes shown in Fig. 6. Each peak and absorption drop was identified by the wave-length determined from the corresponding measured critical voltage substituted in the equation $Ve = hc/\lambda$. Fig. 6 shows that 4 orders of characteristic cesium peaks appear, and in addition the I_β and I_α at 9° 58′ and at 11° 23′. This very striking doubly characteristic spectrum proves at once that it is possible to analyze separately the space distributions of both the cesium and the iodine atoms even more distinctly than in the case of

CsI. From the angles and wave-lengths substituted in the equation $n\lambda = 2d \sin\theta$, d_{100} for cesium is 4.50×10^{-8} cm, and for iodine 1.12×10^{-8} cm. Hence planes containing iodine atoms are ¼ as far apart as those containing cesium atoms.

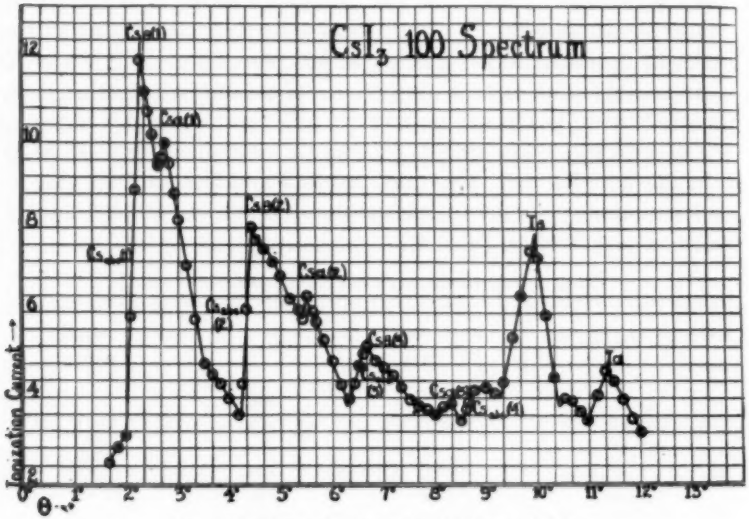

FIG. 6. *Spectrum of reflection by 100 planes of CsI_3.*

The spectra of the 010 and 001 planes duplicate the spectrum of the 100 planes, except that the peaks occur at different angles. A drawing of the 010 spectrum is included in a note in the Proceedings of the National Academy of Sciences.[19] For the 010 planes the first order Cs_β peak appears at 1° 34′ and the I_β peak at 6° 55′. Hence $d_{Cs} = 6.43\times10^{-8}$ cm and $d_I = 1.609\times10^{-8}$ cm. For the 001 planes the first order Cs_β peak is at 1° 26′ and the I_β peak at 6° 21′, with corresponding values of d of 7.02 and 1.76×10^{-8} cm. Analyses of the experimentally determined spectra of the 100, 010, and 001 planes are given, respectively, in Tables 7, 8 and 9.

As a further check we made a determination with the 110 planes at an angle of 34.31° (34° 19′) from the 100 peak. At an ionization chamber angle of 20°, or $\theta = 10°$, the critical voltage was 18,880 volts, corresponding to a wave-length of .639Å. and d of 1.86×10^{-8} cm. But also $d_{110} = \frac{1}{2}\, d_{010} \sin 34° 19' = 1.85\times10^{-8}$ cm.

Since the iodine planes lie ¼ as far apart as the planes containing cesium atoms in all three directions, there is only one space distribution

TABLE 7. *Analysis of the Spectrum of the 100 Planes of CsI_3*

No.	θ	Critical Voltage	λ (from Crit. V.)	Radiation	$d \times 10^8$ cm
1	2° 10′	35 900	.344	Cs_{abs} (1)	4.50
2	2° 14′	35 000	.354	$Cs\beta$ (1)	
3	2° 46′	30 900	.400	$Cs\alpha$ (1)	
4	4° 20′	35 900	.344	Cs_{abs} (2)	
5	4° 26′	(Calcd. 4° 28′)	.352	$Cs\beta$ (2)	
6	5° 30′	(Calcd. 5° 32′)	.400	$Cs\alpha$ (2)	
7	6° 29′	(Calcd. 6° 30′)	.344	Cs_{abs} (3)	
8	6° 40′	(Calcd. 6° 42′)	.352	$Cs\beta$ (3)	
9	8° 18′	(Calcd. 8° 18′)	.400	$Cs\alpha$ (3)	
10	8° 38′	(Calcd. 8° 40′)	.344	Cs_{abs} (4)	
11	9° 58′	31 800	.390	$I\beta$	1.12
12	11° 23′	28 300	.436	$I\alpha$	

TABLE 8. *Analysis of the Spectrum of the 101 Planes of CsI_3*

No.	θ	Critical Voltage	λ (from Crit. V.)	Radiation	$d \times 10^8$ cm
1	1° 32′	35 938	.342	Cs_{abs} (1)	6.43
2	1° 34′	35 100	.352	$Cs\beta$ (1)	
3	1° 47′	30 864	.400	$Cs\alpha$ (1)	
4	3° 4′	35 900	.345	Cs_{abs} (2)	
5	3° 8′	35 200	.350	$Cs\beta$ (2)	
6	3° 34′	30 864	.400	$Cs\alpha$ (2)	
7	4° 36′	35 940	.342	Cs_{abs} (3)	
8	4° 42′	(Calcd. 4° 42′)	.352	$Cs\beta$ (3)	
9	5° 20′	30 860	.400	$Cs\alpha$ (3)	
10	6° 10′	35 950	.342	Cs_{abs} (4)	
11	6° 55′	31 820	.389	$I\beta$	1.609
12	7° 45′	28 270	.437	$I\alpha$	

possible in the unit parallelopiped containing 1 molecule of CsI_3. This unit contains cesium atoms at each corner, and the 3 iodine atoms on the body diagonal at distances of ¼, ½, and ¾ of its length; in other words, an iodine atom lies at the center of the parallelopiped, and one on each side of it, equidistant half-way between the center and a corner cesium atom. There is no evidence that the diagonals are all unidirectional in a crystal.

THE STRUCTURE OF CESIUM IODIDE DIBROMIDE, $CsIBr_2$

For this analysis of $CsIBr_2$ we prepared beautiful orange-red crystals of $CsIBr_2$ by dissolving the theoretical amount of bromine in a solution

TABLE 9. *Analysis of the Spectrum of the 001 Planes of CsI_3*

No.	θ	Critical Voltage	λ (from Crit. V.)	Radiation	$d\times10^8$ cm
1	1° 24′	35 900	.344	Cs_{abs} (1)	
2	1° 26′	35 000	.354	$Cs\beta$ (1)	
3	1° 38′	30 860	.400	$Cs\alpha$ (1)	7.02
4	2° 48′	(Calcd. 2° 48′)	.344	Cs_{abs} (2)	
5	2° 53′	(Calcd. 2° 52′)	.352	$Cs\beta$ (2)	
6	3° 15′	(Calcd. 3° 16′)	.400	$Cs\alpha$ (2)	
7	4° 10′	(Calcd. 4° 12′)	.344	Cs_{abs} (3)	
8	4° 19′	(Calcd. 4° 18′)	.352	$Cs\beta$ (3)	
9	4° 51′	(Calcd. 4° 54′)	.400	$Cs\alpha$ (3)	
10	5° 33′	(Calcd. 5° 36′)	.344	Cs_{abs} (4)	
11	5° 46′	(Calcd. 5° 44′)	.352	$Cs\beta$ (4)	
12	6° 21′	31 840	.388	$I\beta$	1.76
13	7° 3′	28 300	.436	$I\alpha$	

of *CsI*. Wells and Penfield prepared the compound by adding bromine and iodine to a solution of *CsBr*. The crystals, analyzed in the same way as CsI_3, proved to be orthorhombic and hence isomorphous and very closely similar as regards lattice distances to CsI_3. The distances between cesium planes compare as follows:

Plane	CsI_3		$CsIBr_2$	
100	4.50	$\times10^{-8}$ cm	4.26	$\times10^{-8}$ cm
010	6.43		5.91	
001	7.04		6.90	

As an example of the angles between planes, an angle of 49° 24′ separated the 001 and 011 planes.

The spectra of $CsIBr_2$ differ in important respects from those of CsI_3. In the latter case iodine peaks did not appear until after the fourth order peaks of cesium, inasmuch as the iodine planes are only ¼ as far apart as cesium planes. In $CsIBr_2$, however, an iodine plane lies exactly midway between two successive cesium planes. Inasmuch as the characteristic wave-lengths of cesium and iodine differ so little, the tall first order spectrum peak appears quite complex, since it comprises four incompletely separated peaks produced by the characteristic rays of *both* cesium and iodine. In the higher order reflections, however, these peaks undergo a remarkably distinct separation. These facts are well shown by the spectrum of the 100 planes in Fig. 7. Table 10 contains the detailed data. The peak at the top of the first order

absorption drop comes at an angle of 2.50°; the critical voltage was 35,000 volts, corresponding to the wave-length .354Å., the K_β of cesium, and $d = 4.26 \times 10^{-8}$ cm. At 6.47°, between the various second and third order cesium and iodine peaks, a symmetrically shaped tall peak appeared, quite similar in every respect to the I_β peak in CsI_3. If this peak has the wave-length .929Å., the K_β of bromine, d comes out 2.13×10^{-8} cm, i.e., exactly half the value of d_{Cs} and d_I. Thus, even

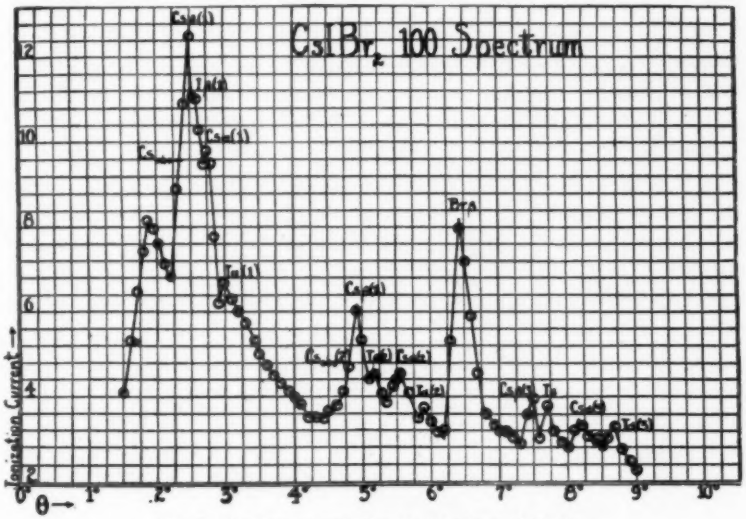

FIG. 7. *Spectrum of reflection by 100 planes of $CsIBr_2$.*

though the analysis of $CsIBr_2$ remains somewhat incomplete, we have detected the characteristic rays of all three elements in this crystal, and hence extended the observation of the excitation of atoms in crystals by the primary beam, their emission of characteristic rays, and the reflection of these rays by the same crystal down to atomic number 35. The atomic distribution in $CsIBr_2$ apparently agrees with that in CsI_3, with the two bromine atoms on the diagonal on either side of the central iodine atom.

The 010 and 001 spectra are similar to the spectrum of the 100 planes. In the first order complex peak of the 010 spectrum Cs_{abs} at 1.67°, Cs_β at 1.71° and I_β at 1.88° were identified and gave as d for Cs and I 5.91×10^{-8} cm. In the first order peak of the 001 spectrum Cs_{abs}, at 1.43°, Cs_β at 1.47°, I_β at 1.60° and Cs_α at 1.71° gave d the value of 6.90×10^{-8} cm. This polyhalide is being subjected to further intensive

investigation, together with $RbICl_2$ and $CsIBrCl$. In the case of the last-named we hope to detect the characteristic radiations of all four elements by a special ionization chamber, devised so as to reduce absorption of the long chlorine rays to a minimum.

TABLE 10. *Analysis of the Spectrum of the 100 Planes of $CsIBr_2$. (Cf. Fig. 9)*

No.	Angle Reading	θ	Angle Reading Calc'd	Critical Voltage	λ	Radiation	d
	24.15°	0°					
1	26.50°	2.35°		35 900	.345	$Cs_{\alpha b\alpha}$ (1)	4.26
2	26.65°	2.50°		35 000	.354	$Cs\beta$ (1)	
3	26.76°	2.61°		32 000	.387	$I\beta$ (1)	4.26
4	26.90°	2.75°		31 166	.397	$Cs\alpha$ (1)	
5	27.08°	2.93°	27.08°		.437	$I\alpha$ (1)	
6	29.00°	4.85°	29.00°		.344	$Cs_{\alpha b\alpha}$ (2)	4.26
7	29.10°	4.95°	29.15°		.352	$Cs\beta$ (2)	
8	29.36°	5.21°	29.35°		.388	$I\beta$ (2)	
9	29.67°	5.52°	29.65°		.400	$Cs\alpha$ (2)	
10	30.04°	5.89°	30.01°		.437	$I\alpha$ (2)	
11	30.62°	6.41°			.929	$Br\beta$	4.26/2
12	31.65°	7.50°	31.65°		.352	$Cs\beta$ (3)	
13	31.85°	7.70°	31.90°		.388	$I\beta$ (3)	
14	32.35°	8.20°	32.40°		.400	$Cs\alpha$ (3)	
15	32.85°	8.70°	32.88°		.437	$I\alpha$ (3)	

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[20] McKeehan, *J. Optical Soc. Am.*, *6*, p. 989; Dec., 1922.

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AN ADAPTATION OF THE THALOFIDE CELL TO THE MEASUREMENT OF PHOTOGRAPHIC DENSITIES*

By Arthur L. Schoen

In photographic research, it is frequently necessary to measure low densities with great accuracy. For example, in the photographic sensitometry of emulsions containing silver grains coated in one layer, the densities of the sensitometric strips are so low that the usual procedure of measuring them with the Martens polarization photometer is inadequate. In fact it is difficult to see with the naked eye any difference in density between successive steps. Photomicrographs of these strips, however, show a difference in the number of exposed silver grains in a given area and hence a small difference in density.

The remarkable sensitivity of the thalofide cell[1] (Fig. 1) to red and infra red radiation suggested that this might be applied as a physical photometer to measure these low densities, provided the conditions for high sensitivity and stability were known, that is, the condition in which the thalofide cell would give its greatest response to a small change in illumination and still be reliable in its action. As pointed out in the above reference, this cell acts like the well-known selenium cell in that its electrical resistance is lowered upon exposure to light. Blue and violet light, however, seem to produce a slow and permanent decrease in the resistance of the cell which makes it necessary to limit the radiation to the red and near infra red region of the spectrum by means of a red filter.

The literature on the subject of photosensitive materials is now quite extensive[2] and a study of this indicated many ways of using the thalofide cell in a physical photometer. After several trials of various possible circuits,[3] the following was adopted (see Fig. 2) as the most suitable for our purpose. The thalofide cell *C* mounted in a light tight box with a small window at A was connected in series with a battery *B* and a sensitive galvanometer *G*.[4] The auxiliary circuit[5] *D E F* shunting the galvanometer was used to annul the effect of the "dark current" through the cell and also formed a convenient means of adjusting the galvanometer to zero when illuminated. A small automobile lamp *L* operated from a storage battery served as the source of illumination and was arranged to move along the graduated track *T*.

* Communication No. 171 from the Research Laboratory of the Eastman Kodak Company.

The first test was made for the purpose of finding what effect a change in the impressed voltage would have on the dark current in the unilluminated cell. The auxiliary circuit was disconnected and the voltage of the battery *B* increased step by step to about fifty volts. The deflections of the galvanometer were plotted against the corre-

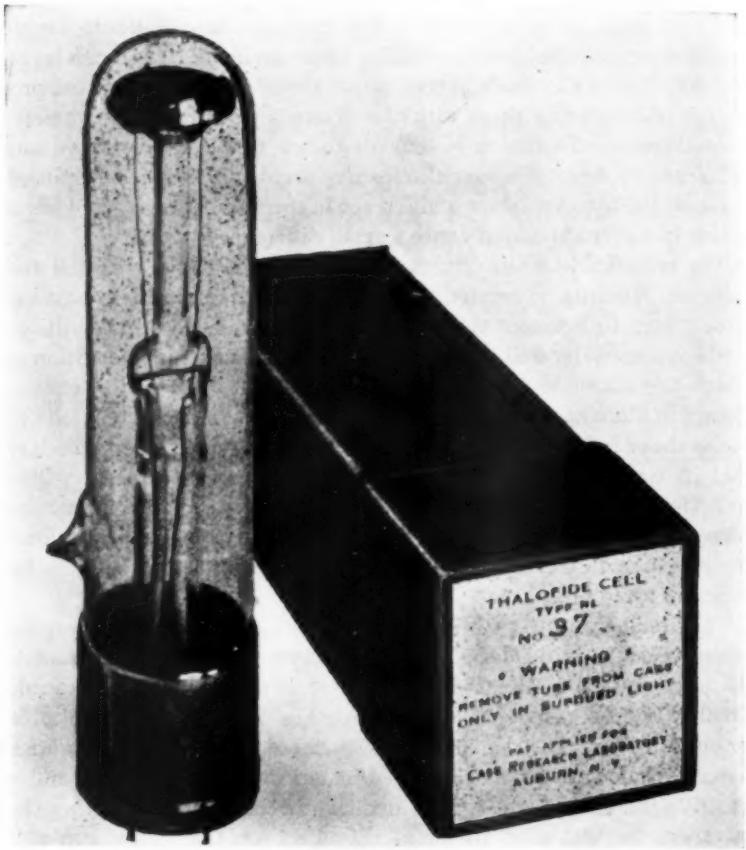

FIG. 1. *Thalofide cell.*

sponding voltages. Fig. 3 shows that for this particular cell a small change in voltage above 40 volts would produce a considerable change in the galvanometer deflection. In addition, it was observed that

above 40 volts the galvanometer continued to drift slowly to larger scale readings, indicating a slow decrease in the resistance of the cell.

Trials of several different methods of using the thalofide cell for the measurement of density indicated that the most satisfactory results were obtained by the use of a null method involving constant illumination of the sensitive surface of the cell. In the method adopted,

FIG. 2. *Diagram of electrical circuits.*

the galvanometer reading was reduced to zero after the insertion of the unknown density over the window *A* (Fig. 2) by adjusting the light so that the illumination on the sensitive surface was the same as that used in making the initial adjustment. This illumination on the sensitive surface will be referred to as the "basic illumination." Since it

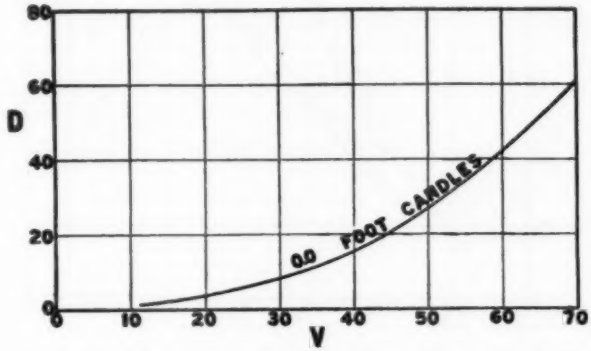

FIG. 3. *Relation between "dark current" and voltage across cell.*
D = galvanometer deflection.
V = voltage across cell (B Fig. 2).

was desirable to determine the value of voltage across the cell which would result in a relatively large galvanometer deflection for a small change in the basic illumination, a series of measurements were made. The lamp *L* was adjusted to illuminate the cell *C* to about 0.13 f.c. The potential across the terminals of the cell was set at a value of 10

volts, and by means of the auxiliary circuit the galvanometer deflection was reduced to zero. Then a photographic density was placed over the window A and the resulting deflection of the galvanometer recorded. This procedure was repeated for increasing cell voltages up to 60 volts and the curve marked 0.13 foot candles in Fig. 4 was plotted from

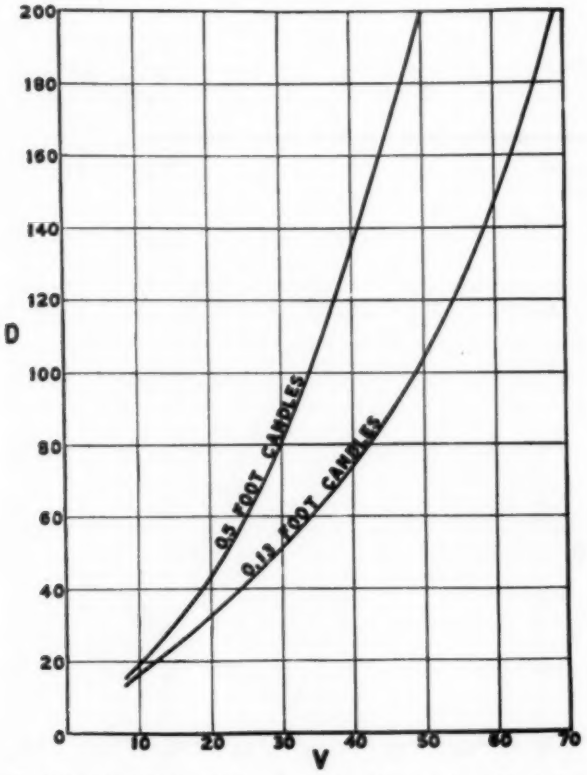

FIG. 4. *Variation of sensitivity with impressed voltage for two values of basic illumination. D = galvanometer deflection for 37% decrease in basic illumination. V = impressed voltage (B Fig. 2).*

these data. This curve shows the deflection given by the galvanometer when the intensity is decreased from 0.13 foot candles to 63% of 0.13 foot candles by means of the added density. A similar curve was obtained for a basic illumination of 0.5 foot candles. It should be noted here that these two curves differ from Fig. 3 in that the

ordinates are deflections of the galvanometer produced by decreasing the basic illumination on the cell 37% by means of the photographic density. These curves show that for the same decrease in illumination the deflection increases as the voltage on the cell increases.

A third test was made in a manner similar to the preceding test in which the voltage on the cell was maintained at 30 volts and the

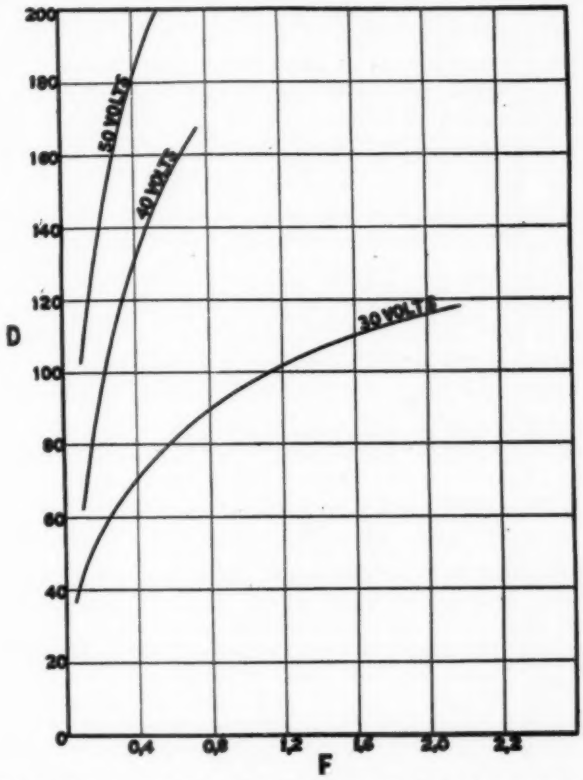

FIG. 5. *Relation between sensitivity and basic illumination for the three values of impressed voltage.*
D = galvanometer deflection for 37% decrease in basic illumination.
F = basic illumination.

basic illumination was increased step by step from 0.1 to 2 foot candles. This was repeated for 40 and 50 volts. Fig. 5 plotted from these data shows that the deflections of the galvanometer produced when the photographic density was put over the window increased for increasing

values of illumination and it would appear as though the best conditions for operation would be a high illumination and a high voltage on the cell. However, as previously stated, a voltage above 40 seems to produce a slow decrease in the resistance of the cell and a relatively high illumination makes the period of recovery too long.

From a study of these curves, it was decided to adjust battery B to 40 volts (or less) for this particular cell and the illumination on the cell to about $0.3\pm$ foot candles. Also the precaution was taken to illuminate the cell for 10 or 15 minutes before measurements were made to permit the cell and battery circuits to come to equilibrium.

After the conditions which it was thought would give the most satisfactory performance had been determined by the above procedure, the various factors were adjusted and a set of sensitometric strips were obtained and measured to test the performance. The set of strips chosen were obtained from Mr. A. P. H. Trivelli of this laboratory and were made by exposing single grain-layer plates, such as he is using in an investigation of the latent image, to the action of X-rays. Since but a single layer of silver grains was available the maximum density was relatively low (approximately 0.2) and the density difference between successive exposure steps was very small. Such a set of strips was therefore, ideal for testing the performance of this instrument.

The auxiliary circuit was adjusted for zero setting of the galvanometer with an unexposed part of the sensitometric strip over window A. The distance d from lamp L to cell C was measured. Then the first step of the sensitometric strip was placed over A and the lamp L moved toward cell C until the galvanometer again read zero. The new distance d_1 was recorded. From the two distances d and d_1 and the inverse square law the transmission $T=\frac{d_1^2}{d^2}$ of the first step was computed. The density of the first step was computed from $D=\log\frac{1}{T}$. In like manner each step on the strip was measured. In Fig. 6 the average of the densities from several strips was plotted in the usual manner against the logarithm of the exposure producing them.[6] It may be of interest to point out that plotting these values as a function of the exposure instead of log exposure the curve in Fig. 7 is obtained.

The tabulated data for this figure (Table 1) showed a considerable variation in the density readings of corresponding steps in the sensitometric strips but this is due almost entirely to variations in the one

grain layer emulsion and to inability to hold the current in the lamp constant with the present equipment. Repeated measurements on the same strips checked very closely.

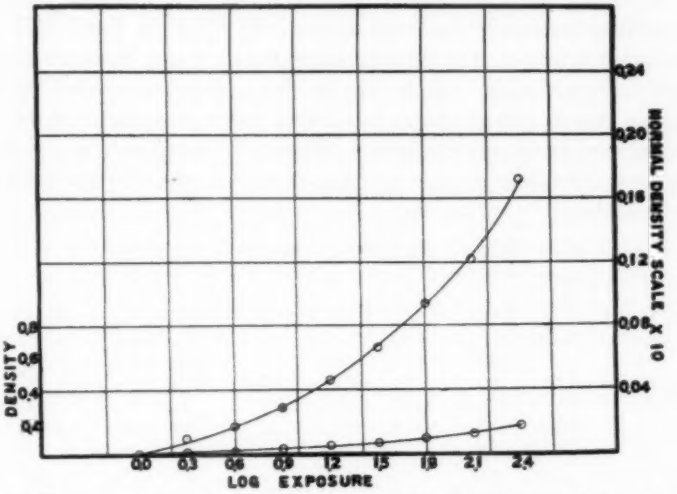

FIG. 6. *Characteristic curve of a one grain layer emulsion with density plotted as a function of log exposure.*

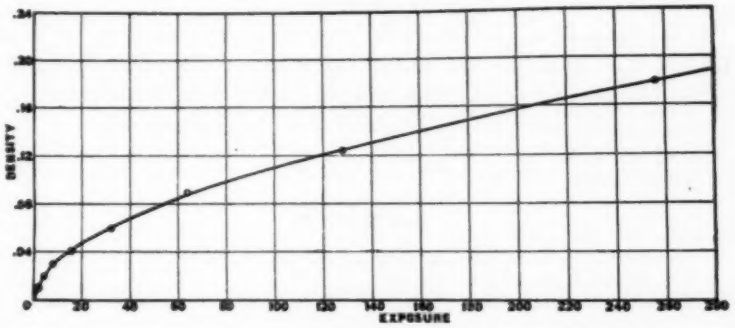

FIG. 7. *Characteristic curve of a one grain layer emulsion with density plotted as a function of exposure.*

It is felt that the results obtained thus far indicate that this method can be used with advantage in problems involving the measurement of very low density and small density differences and that densities as low as .005 ($\pm 99\%$ transmission) can be measured with a fair degree of

certainty. It is thought also that greater refinement may still further increase the sensitivity obtainable. The work reported in this paper was done with an assembly of apparatus available in the laboratory, the assembly being somewhat imperfect and of a temporary nature. A complete instrument has been designed by Mr. L. A. Jones, however, in which it is proposed to assemble all of the necessary elements making a self-contained unit. Great care has been taken to provide the best possible optical and electrical conditions and means provided for convenient and rapid manipulation. When this instrument is complete, it is hoped to obtain greater precision than was given by the preliminary assembly.

TABLE 1. *Density Measurements on Strip No. 6*

Step	Test 1	Test 2	Test 3	Average
1	.000	.000	.000	.000
2	.013	.019	.017	.016
3	.028	.028	.028	.028
4	.035	.035	.038	.036
5	.050	.052	.050	.050
6	.076	.075	.071	.074
7	.106	.103	.104	.104
8	.141	.148	.138	.142
9	.189	.202	.184	.191

It is a pleasure at this time to express my indebtedness to Mr. L. A. Jones of this laboratory for many helpful suggestions and co-operation in the development of this work and also to Mr. T. W. Case of the Case Research Laboratory for the illustration of the thalofide cell.

ROCHESTER, N. Y.
JANUARY, 1923.

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U. S. Patents 1, 301 227 and 1 316 350.
Bureau of Standards Scientific Paper No. 380. Spectrosphotoelectric Sensitivity of Thalofide.
Prof. J. C. McLennan and W. W. Shaver, Proc. Roy. Soc., *100*, pp. 200–217, Nov. 1, 1921.
[2] Scientific Papers, Bureau of Standards, No. 319–398 and references listed there.
[3] Scientific Paper, Bureau of Standards, No. 319 and references listed there.
[4] Leeds and Northrup High Sensitivity Galvanometer Resistance 425 ohms. Sensitivity 14 740 megehms. Scale distance = 1 meter.
[5] Physical Review, *34*, p. 370; 1912.
[6] The Photographic Rendering of Tone Values. By L. A. Jones Jour. Frank. Inst., April, 1920; p. 469.

A DIRECT READING BURETTE[1]

By Albert M. Jackson

The device here described is designed for use in laboratories where the work is largely of a routine nature, that is, where the same tests are made every day and where the chemist knows approximately what the results should be. In such laboratories the standard solutions are made to such a strength that a very small amount, say 1 to 3 cc's, suffices for a single test. Hence an ordinary 50 cc burette is filled but once for about 15 tests, and after the first test, the chemist must subtract the two readings to find the exact number of cc's used. This introduces a possibility of error, due to mistakes made when subtracting, and also requires time.

The Direct Reading Burette gives a direct reading for each titration, hence no subtraction is necessary and errors are eliminated.

This burette is produced by the following method:

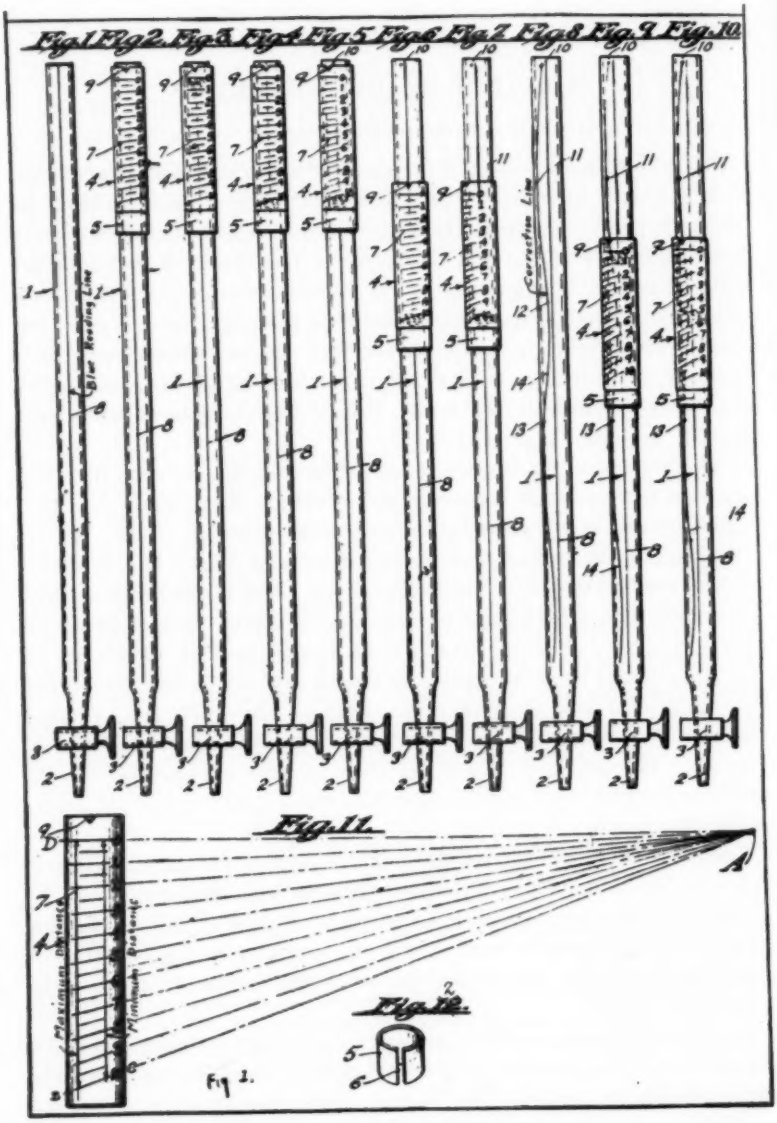
A regular 50 cc ungraduated burette (Shellback Type), Fig. 1, having the blue reading line (8) at the back, is used. This is filled with distilled water and 10 cc's by weight are let out; the linear distance along the burette occupied by these 10 cc's is measured; another 10 cc's are let out, the distance again measured, and so on until the burette is emptied. The maximum and the minimum distances are noted and are then laid out on two parallel lines about a half an inch apart as shown on Fig. 11. The points *B* and *C* are then joined by a line and the line produced until it intersects the line *DA* (which is drawn at right angles to the two parallel lines) at the point *A*.

Lines are then drawn from the point *A* cutting the parallel lines at 100 equidistant points, each division representing .10 of a cc.

These converging lines are then marked off on a glass tube, having such an inside diameter that it will fit snugly over the burette. A metal split ring (Fig. 12) is then placed on the burette to support the glass slide.

A notch (9) is cut on the upper end of slide and the slide placed on the burette. The burette is again filled with distilled water and the slide is moved up or down the burette (being moved by pushing the metal clip up or down) until the zero line is at the level of the liquid

[1] U. S. Patent No. 1386571; Aug. 2, 1921.



FIGS. 1 to 12. *Standardizing burette.*

(Fig. 3). 10 cc's are then let out by weight. The slide is then turned right or left (being supported at the same elevation by the metal clip) until the 10 cc line intersects the point of liquid opposite the blue reading line. A mark (10) is now made on the burette in the notch at the top of the slide (Fig. 5).

The slide is now moved down the burette until the zero line is again opposite the level of the liquid (Fig. 6), 10 cc's are let out and the slide revolved until the 10 cc line again intersects the point of liquid and another point (11) is marked on the burette in the notch (Fig. 7). This procedure is repeated until the entire 50 cc's are let out and 5 points are spotted on the burette. These points 10, 11, 12, and 13 are then joined by lines, the whole forming a correction line (14).

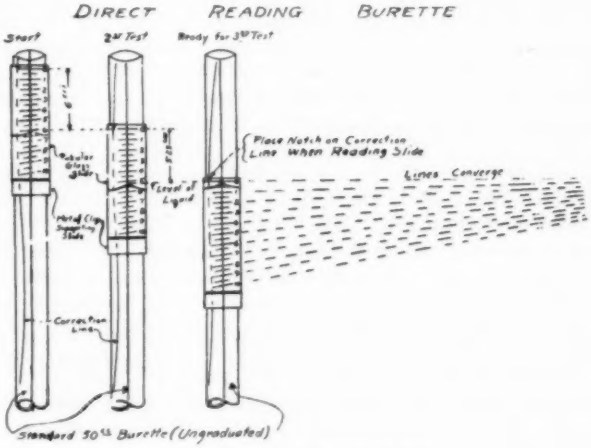


FIG. 13. *Making a series of tests.*

In using the Direct Reading Burette for making a series of tests, Fig. 13, the chemist fills the burette with the standard solution, moves the slide up or down until the zero line is at the level of the liquid, makes his test and then revolves the slide right or left, until the notch is at the correction line, and then reads the slide at the point of liquid in front of the blue reading line. The slide is then moved down the burette until the zero line is again opposite the point of liquid and the second test is made, the slide revolved as before until the notch is on the correction line and the direct reading made. This procedure is repeated until the burette is empty, or the tests completed.

On the Direct Reading Burette the lines on the slide are made to converge, so as to compensate for variations in the internal diameter of the burette.

It is not possible to graduate the slide with parallel lines owing to variations in the cross sectional area of the burette. If the graduation on a standard 50 cc burette are measured, the distance between the 0 and the 10 cc marks and between the 40 cc and 50 cc marks may vary as much as .20 of a cc.

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On the Richardson Gyro-Magnetic Effect.—If ferro-magnetism is due to the presence of revolving particles of mass m and charge e then the sum of their angular momenta, P, divided by the magnetic moment they produce, M, is equal to $2m/e$. (See Richardson, Phys. Rev., *26*, p. 248, 1908; or Sommerfeld's Atombau, 3rd edition, pp. 304 ff.). When the magnetization is changed, a reactive impulse is communicated to the body of which the charges form a part, such that $\Delta P = \Delta M \cdot 2m/e$. If the charges are electrons, the ratio $\Delta P/\Delta M$ $(=R)$ should be 1.13×10^{-7} in *e.m.u.*, but experiment gives about 0.5 of this value. There are 3 methods of experiment: (1), the specimen is hung inside a magnetizing helix by a quartz fiber, and is turned by the impulse when the circuit is momentarily closed; (2), identical with (1) save that the magnetizing current is applied at intervals of time equal to the period of oscillation of the specimen, so that a large deflection is built up by resonance; (3), a null method now being developed by the authors; the repeated impulses are balanced by simultaneous *exterior* impulses applied in the opposite direction.

The present paper describes very careful experiments made by method (1). M was measured by a magnetometer. Errors due to earth's field, to non-coincidence of the axes of magnetic moment and of oscillation in the specimen, etc., were compensated as far as possible, the residual effects being allowed for. It was shown that the low value of R is *not* due to time lag in communication of the impulse from the electrons to the specimen as a whole. This does not dispose of the possibility that some of the impulse is expended in causing spin of comparatively large aggregates of particles within the specimen. Eddy currents in the specimen have no appreciable effect on the results. R is actually a constant over the whole range of magnetic moments utilized. The results of four series of measurements are: for iron, $R/(1.13\times10^{-7}) = 0.507,\ 0.501,\ 0.500$; for nickel, $R/(1.13\times10^{-7}) = 0.505$. The mean is 0.5, within 6/10 %. [A. P. Chattock and L. F. Bates. Phil. Trans. A, *311*, pp. 257–288; 1922.]

ARTHUR E. RUARK

THE VACUUM GRATING SPECTROGRAPH

By Theodore Lyman

There are four requirements which the design of a vacuum grating spectrograph must satisfy; first, the apparatus must be air-tight; second, the volume must not be too great; third, the methods of reaching the inside of the instrument for the purpose of adjusting the grating or renewing the photographic plate must be as convenient as possible, always provided they do not endanger the first requisite; and fourth, matters must be so managed that the source of light can be brought sufficiently near the slit to illuminate the whole surface of the grating without materially changing the canonical arrangement of the optical parts.

Nearly all vacuum spectrographs are much alike; slit, photograph plate and grating are fixed in position and lie on the circle whose diameter is the grating's radius of curvature; to economize space the slit is usually placed not far from the intersection of the normal to the grating with this circle. The container is often a drawn metal tube, closed at each end by a suitable plate. The first requirement is met by the use of gaskets of soft rubber, leather, and soft wax, or by seals of hard wax; to satisfy the third, one is tempted to employ movable conical joints; in practice, however, they have proved unsatisfactory because of the difficulty of making them air-tight.

The chief adjustments are usually accomplished by moving the grating along the axis of the spectrograph and by turning it about horizontal and vertical axes, the details of the mounting which will permit these motions need not detain us. It is important to note, however, that the slit and plate holder should not be absolutely fixed.

In the case of most of the instruments in actual use detailed descriptions with dimensions are lacking. Millikan's[1] spectograph was intended for the investigation of the radiations from the spark in high vacuum. The source is placed within the body of the instrument directly in front of the slit, this procedure, though excellently adapted to the purpose for which it was intended, is not particularly suited for general spectroscopic investigation. McLennan[2] has placed his source in an air-tight vessel lying entirely outside the spectrograph while the

[1] Physical Rev., *12*, p. 168; 1918.
[2] Proc. Roy. Soc., *98*, p. 115; 1920.

slit and photographic plate are well within the body of the instrument; the arrangement may well violate our fourth requirement, for it must be difficult to bring the source sufficiently near the slit to cover the grating. Hopfield[3] has made a departure from the usual tubular form of the container, he employs a sector-shaped box of cast brass. The innovation in shape has its advantages for it gives more room for the adjustment of the optical parts, the employment of castings, however, is not to be recommended in vacuum apparatus.

Adam Hilger & Co.[4] have placed a vacuum spectroscope on the market, whose appearance is somewhat suggestive of a design due to Paschen. Here the plate holder is inserted through a ground joint into a horizontal casting protruding from a fixed face-plate which closes one end of a tubular container. The slits, two in number, are placed below the plate holder and in the same protruding casting with it. The chief adjustments are made by moving the grating, access to which is gained through a movable face-plate. A horizontal tube communicating with the body of the spectroscope affords a means of introducing a drying agent. The instrument appears to satisfy all four of the standard requirements.

My earlier spectroscopes suffered from two defects: *first*, it was very difficult to get the light source sufficiently near the slit; and *second*, the use of a ground plug through which the plate holder was introduced sometimes gave rise to slight leaks. The instrument with which I am now at work is free from these defects, it still possesses some faults but as no account of it has appeared in print a somewhat detailed description may be useful.

The body, designed to accommodate a grating of 50 cm radius and with a ruled surface of about 5×3 cm, is made of drawn brass tubing 9 cm internal diameter, at each end it is fitted with a flange. The end designed to hold the grating is closed by a circular plate ground to the flange, the joint is made air-tight by a ring of soft wax. The joint at the other end of the apparatus is semi-permanent, flange and plate being held together by Khotinski cement or some sealing wax of the same character. The mounting of the grating within the apparatus presents nothing new, the arrangement of slit and plate holder however are somewhat unusual. The slit is carried in a tube T (Fig. 1), projecting from the permanent face-plate, the manner in which it is mounted

[3] Physical Rev., *20*, p. 573; 1922.
[4] Proc. Roy Soc., *102*, p. 484; 1923.

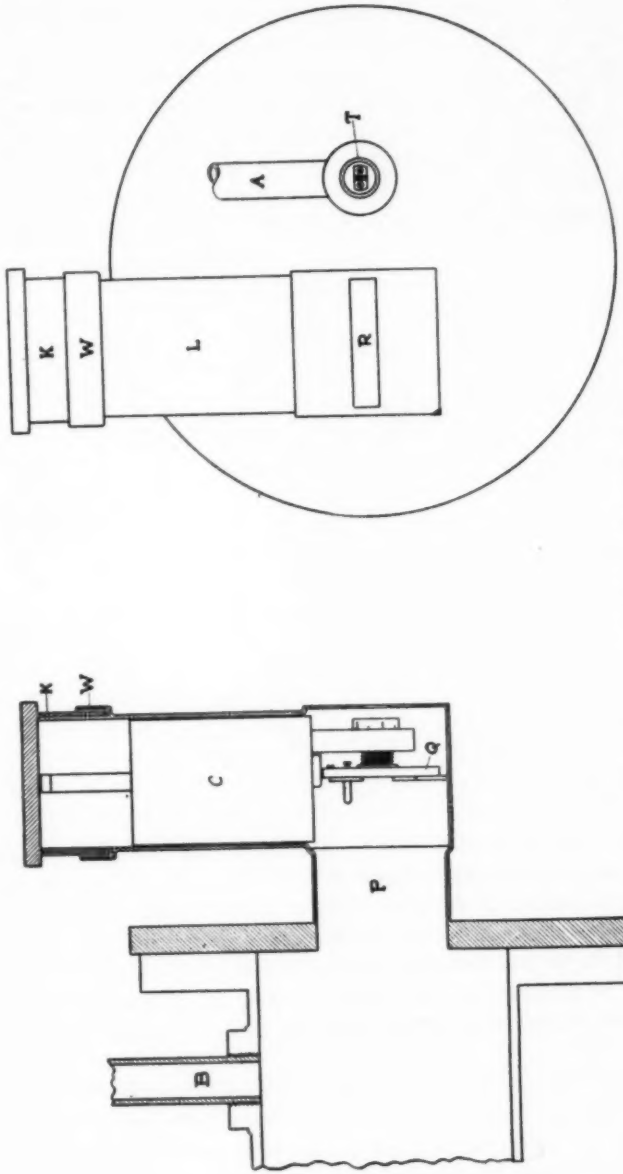

FIG. 1. *Side and front elevation of the plate and slit end of vacuum spectrograph.*

will be given presently. The photographic plate occupies the end of a separate tube P (Fig. 1); it is slipped into position by a vertical motion down the tube L (Fig. 1). The plate holder consists of a cylinder C (Fig. 2) fitting inside L, provided at one end with a handle by which it may be moved, and at the other end by a plate Q which, in turn, carries clips into which the photograph plate 4 cm long by 1 cm wide is fitted (Fig. 2); Q is so mounted with respect to C that the photographic plate may be moved two or three millimeters

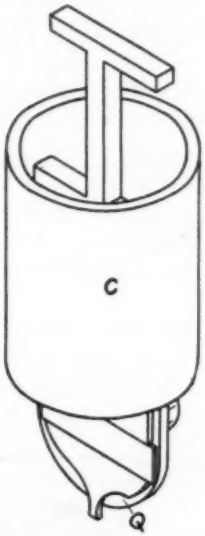

FIG. 2. *Detail of plate carriage.*

toward or away from the grating. Motion of the cylinder C about a vertical axis provides an adjustment for the inclination of the plate. The tube L carries at its upper end a collar W destined to hold a quantity of sealing wax, the cap K slips over L, and rests with its lower edge in W, the wax, melted by a moderate heat, seals the joint air-tight. A window R at the junction of P and L is intended to facilitate the preliminary adjustments, it is ordinarily closed light-tight by a cap.

The vessel which contains the source of light is sealed over the tube T; if the same gas pressure is to be maintained in the vessel and in the body of the spectroscope, they are connected in parallel to the pumping system. In this case the simplest arrangement is to have the slit carried

on a suitable light-tight diaphragm which slips inside T. On the other hand, if the spectroscope is to be maintained at a much lower pressure than the vessel containg the source, it is important that the slit should be short and narrow and that all leaks around it should be prevented. To this end the slit S, .15 mm high and .03 mm wide, forms the only opening in the plate which closes the tube V, this tube slips over T (Fig. 3) and is sealed air-tight. The pump tube A is placed on the grating side of the slit and is destined to remove the gas from this part of the system as rapidly as possible; the body of the spectroscope is exhausted through B (Fig. 1).

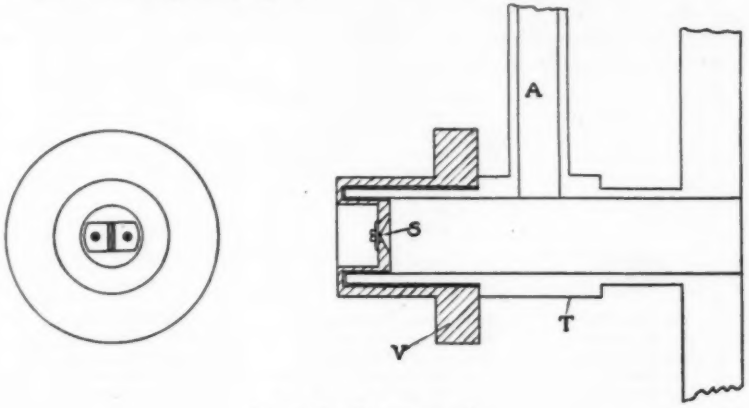

FIG. 3. *Detail of slit mounting.*

In the study of the spectra of gases it is often desirable to reduce the absorption in the discharge tube to a minimum, in this case a tube of the internal capillary type is employed; it is sealed over the tube V in such a manner that the end of the capillary is only a few millimeters from the slit; it is exhausted by a separate pump connection.

The optical adjustment of a vacuum spectrograph is always a tedious business, the instrument just described is no better than some others in point of convenience; it has the advantage however that it can be made perfectly air-tight without undue labor, and it is so designed that the grating may be used at full aperture. Moreover, it is so constructed that absorption, not only within the spectroscope but also within the vessel containing the source, may be reduced to a minimum.

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HARVARD UNIVERSITY,
MARCH, 1923.

Official Abbreviations of International Metric Units.—So many inquiries have been made concerning metric abbreviations that the official list used by the Bureau of Standards conformably to the principle followed in the abbreviations adopted by the International Committee on Weights and Measures, October 2, 1879, will be of interest to the readers of this Journal (See Procès-Verbaux des Séances de 1879, Comité International des Poids et Mesures; vol. 4, p. 41; 1880.)

This action was taken under the Metric Treaty of 1875, now signed by 28 nations. Under the terms of this treaty these 28 nations jointly maintain the International Bureau of Weights and Measures, and entrust the administration of this Bureau and of the metric system to an official International Committee on Weights and Measures. The system of abbreviations was referred to all the Treaty nations and adopted after their official approval.

PREFIXES	UNITS
k kilo-	m meter
h hecto-	g gram
dk* deka-	l liter
d deci-	a are
c centi-	
m milli-	

LINEAR (length)	SQUARE (area)	CUBIC (volume)
km kilometer	km^2 square kilometer	km^3 cubic kilometer
hm hectometer	hm^2 square hectometer	hm^3 cubic hectometer
dkm dekameter	dkm^2 square dekameter	dkm^3 cubic dekameter
m meter	m^2 square meter	m^3 cubic meter
dm decimeter	dm^2 square decimeter	dm^3 cubic decimeter
cm centimeter	cm^2 square centimeter	cm^3 cubic centimeter**
mm millimeter	mm^2 square millimeter	mm^3 cubic millimeter
μ micron (=0.001 mm)	μ^2 square micron	μ^3 cubic micron

MASS*** (weight)	SURFACE (land area)	CAPACITY (of containers)
kg kilogram		kl kiloliter
hg hectogram	ha hectare	hl hectoliter
dkg dekagram		dkl dekaliter
g gram	a are	l liter
dg decigram		dl deciliter
cg centigram	ca centare	cl centiliter
mg milligram		ml milliltier**

A similar plan is used by the Bureau for abbreviations of cgs units and others. mf millifarad (m milli, f farad); μf microfarad; mμ a thousandth of a micron, and $\mu\mu$ one millionth of a micron. (See Guillaume: Unités et Étalons, p. 7, note.)

* "dk" suggested and used by Bureau to distinguish from "d."
** "cc" is often used.
*** "t" = metric ton = 1000 kg.

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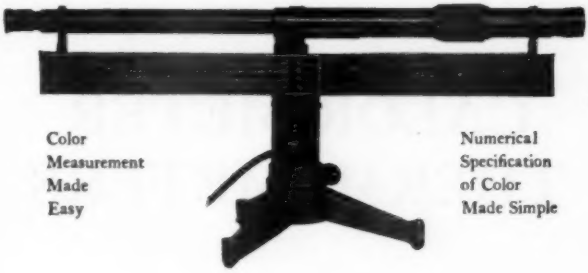

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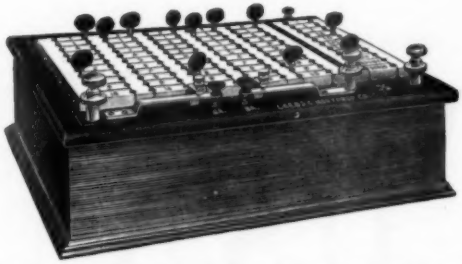

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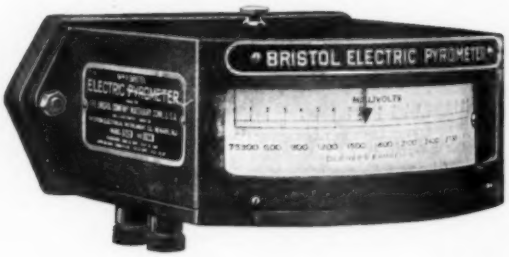

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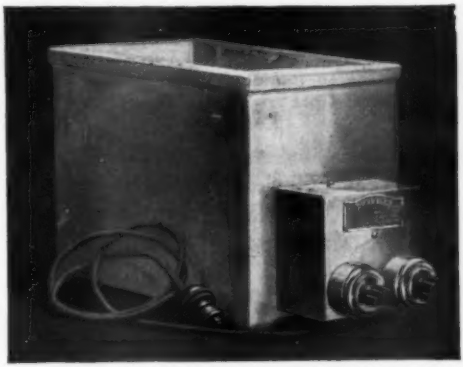

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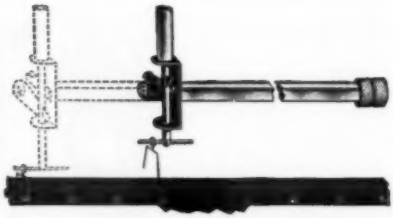

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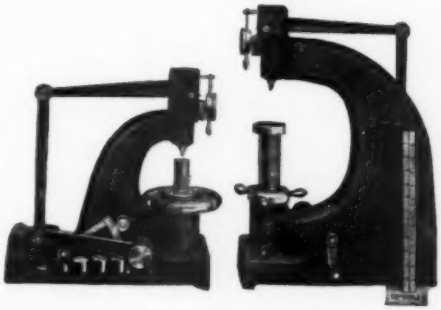

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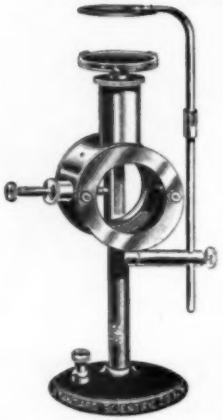

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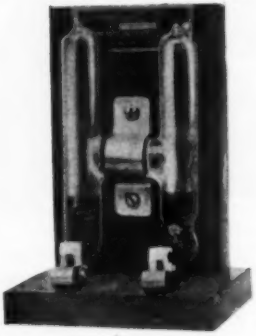

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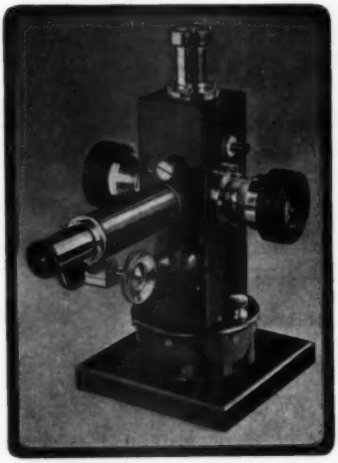

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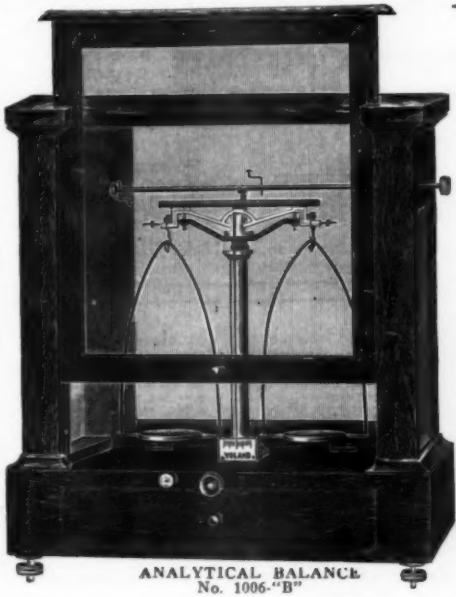

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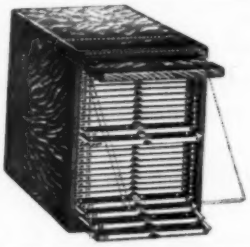

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